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INVESTIGATION OF THE MECHANISM OF POLYCONDENSATION OF 1,3-DICHLOROBUTENE-2 IN THE PRESENCE OF FRIEDEL – CRAFTS – GUSTAVSON CATALYSTS. I.

A. L. Klebanskii, A. G. Saiadian and M. G. Barkhudarian

Polycondensation of 1,3-dichlorobutene-2 under the influence of Friedel – Crafts – Gustavson catalysts has been described in the Authors Certificate by Akopian, Saiadian and Barkhudarian [1]. No other literature data on this problem are available. Polymers of 1,3-dichlorobutene-2 are of interest as film-forming substances. In addition, polycondensation of 1,3-dichlorobutene-2 simulates in large measure the vulcanization of polychloroprene under the influence of metallic oxides.

We have investigated the polycondensation of 1,3-dichlorobutene-2 in the presence of $AlCl_3$, $FeCl_3$, $ZnCl_2$ and $SnCl_4$.

In all cases we found that low-molecular weight compounds were formed as well as resinous products. Polycondensation proceeds with the greatest efficiency in the presence of $AlCl_3$, with the formation of high-molecular weight polymers as the main products of the reaction. With $FeCl_3$ the process is slower and this gives rise to the formation of low-molecular weight products in considerable yields. $ZnCl_2$ approaches $FeCl_3$ in catalytic activity.* Dimers as well as low-molecular weight polymers were isolated from the reaction products. In the course of the examination of the composition and structure of the low-molecular weight constituents it was found that these contained the dimer ($C_8H_{12}Cl_4$) and a substance having the composition $C_8H_{11}Cl_3$.

At the present time, reactions catalyzed by Friedel – Crafts catalysts are interpreted in terms of an ionic mechanism involving the participation of so-called carbonium ions [2,3]. The mechanism of this reaction is considered in terms of the formation of addition complexes between the catalyst and the olefins. In the case of the molecule of 1,3-dichlorobutene-2 the shift of electron density brought about by the positive inductive effect of the methyl group and the conjugation of π-electrons of the double bond with the unpaired electrons on the chlorine atom renders the chlorine atom in position 1 highly reactive. The enhanced lability of this chlorine atom in its turn facilitates the formation with Friedel – Crafts catalysts of the complex $CH_3-CCl=CH-CH_2^+ \cdot FeCl_4^-$. The latter adds on to dichlorobutene according to the scheme

$$FeCl_4^- + CH_2^+-CH=CCl-CH_3 + CH_3-CCl=CH-CH_2Cl \longrightarrow$$

$$\longrightarrow CH_3-\underset{\displaystyle FeCl_4}{\underset{|}{C}}Cl-\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}-CH_2-CH=CCl-CH_3 \longrightarrow$$

(I)

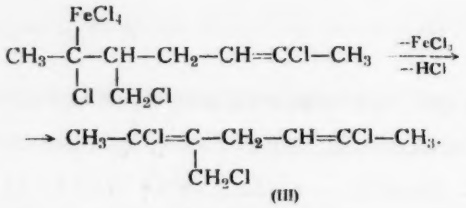
$$\longrightarrow CH_3-CCl_2-\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}-CH_2-CH=CCl-CH_3 + FeCl_3$$

(II)

*The problem of the relative efficiency of different catalysts and of their influence on the yield of low- and high-molecular weight products resulting from the polycondensation will be discussed in greater detail in connection with our investigation of the preparation of film-forming substances based on polymers of 1,3-dichlorobutene-2.

The dimer, 2,6,6-trichloro-5-chloromethylheptene-2, has, in fact, the structure (II) which has been proved by ozonolysis. In the decomposition products of the ozonide we have found acetic acid (80% of the theoretically possible amount), β-chloromethyl-γ-dichlorovaleric acid (62.9%) and hydrochloric acid (91%).

The substance with the formula $C_8H_{11}Cl_3$ is apparently formed as a result of the simultaneous splitting of $FeCl_3$ and HCl from the complex



(III)

Among the products of ozonolysis of the substance $C_8H_{11}Cl_3$ we found acetic acid (80% of theory), hydrochloric acid (79.8%), chloroacetone (83.7%) and carbon dioxide (84%). The latter compounds are the products of the decomposition of γ-chloroacetoacetic acid which has not been isolated because of its instability. On the basis of these data it may be accepted as proved that the substance has the structure (III), i.e. the splitting off of HCl involves the tertiary carbon atom. The dimer of 1,3-dichlorobutene-2 (II) was polymerized in the presence of $FeCl_3$. In addition to various polymers, compound (III) was isolated from the reaction mixture.

The identity of 1,3-dichlorobutene-2 formed in the polycondensation as well as that of the products of the combination of two molecules, formed through the splitting off of HCl under the influence of $FeCl_3$, has been fully confirmed by analysis and ozonolysis. These results show that polycondensation of 1,3-dichlorobutene-2 takes place in a step-wise manner: first, there is combination of two molecules of 1,3-dichlorobutene-2, followed by the splitting off of HCl from the dimer (II); the resulting unsaturated compound (III) combines with a second molecule of 1,3-dichlorobutene-2; this is again followed by the splitting off of HCl with the formation of a new unsaturated compound, and so on. However, these results still only give an incomplete picture as regards the direction of the addition of the catalyst and of the nature of the splitting off of HCl from polymers of higher molecular weight.

The polymer distribution was determined by fractional precipitation with methanol from benzene solution. Among the products of decomposition of the ozonides of these fractions we detected carbon dioxide, acetic acid and a resinous product the structure of which could not be established. In view of the fact that with increasing complexity of the molecules the number of possible directions of the combinations of these molecules increases, it was found necessary to abandon the investigation of the structure of the high molecular weight products and to limit the investigation to the separation of these polymers into narrow fractions which were submitted to detailed analysis. The results obtained, from the investigation of the structure of compounds found by polycondensation of 1,3-dichlorobutene-2 under the influence of Friedel-Crafts catalyzates, provide a basis for the interpretation of the mechanism of vulcanization of polychloroprene under the influence of metallic oxide. As has been demonstrated in a number of investigations [3, 4], vulcanization of polychloroprene proceeds through the interaction of the allylic chlorine formed as a result of 1,2-addition (followed by isomerization of the tertiary chlorine atom into an allylic one) to the metallic oxides (MgO, ZnO, Fe_2O_3, etc.). Monomer units containing allylic chlorine amount to 1.5-2% of the polymer.

The mechanism of the vulcanization of polychloroprene is at present still insufficiently understood. It might be thought that this mechanism is based on the formation of an oxygen link between individual chains as a result of the interaction of allylic chlorine in molecules of the polymer with metallic oxides. However, the above experimental data on the polycondensation of 1,3-dichlorobutene-2 which contains allylic chlorine as well as a chlorine atom attached to a double bond carbon atom, give reasons to suppose that vulcanization of polychloroprene proceeds only partially through an oxygen bridge, and this only in the initial stage of the reaction. The subsequent mechanism is a polar one taking place under the action of the metallic chlorides formed ($ZnCl_2$, $FeCl_3$, etc.), with the formation of C — C bonds between polymer chains in accordance with the same mechanism which is operative in the case of the polycondensation of 1,3-dichlorobutene-2, i.e. through the addition of carbon atoms with an allylic chlorine in one chain to the double bonds of a second molecule, followed by the splitting off of HCl which gives rise to the formation of $ZnCl_2$.

EXPERIMENTAL

254 g of 1,3-dichlorobutene-2 was heated on an oil bath at the boiling point during 14 hours in the presence of 0.825 g of $FeCl_3$. The reaction was accompanied by the evolution of HCl. On fractionation in vacuo, after previous separation of unreacted 1,3-dichlorobutene-2, the following fractions were obtained: fraction 1, 80-100°/5 mm, 22.84 g; fraction 2, 100-115°/5 mm; residue polymer, 25.3 g. After a second distillation of fraction 1 there was obtained 9.2 g of compound (I) boiling at 91-93°/5 mm.

d^{20}_4 1.189, $n^{20}D$ 1.500, MR_D 52.71; Calculated, 52.90

Found, %: Cl 49.16, Cl (saponifiable) 16.40. $C_8H_{11}Cl_3F$. Calculated, %: Cl 49.88, Cl (sapon.) 16.62. Unsaturation was determined with 0.1 N bromine solution in chloroform. Found, 1.436 g Br_2 per 1 g of compound. Calculated 1.497 g Br_2.

6.84 g of compound (I) was taken for ozonolysis. Ozonolysis was carried out in solution in purified chloroform at -20°. On decomposing the reaction product with water there was evolution of CO_2 which was absorbed in 1 N solution of $Ba(OH)_2$; there was obtained 4.009 g of barium carbonate, which corresponds to 0.894 g of CO_2. The ozonolysis product passed almost entirely into solution in water, with the exception of a small amount of a resinous substance (0.1 g). Water was removed in vacuo (58 – 60° at 150 mm); and the residue contained 0.13 g of resin, making a total of 0.25 g. The acids contained in the aqueous distillate (174.4 g) were then determined. Total acidity was equivalent to 5.66 g KOH. No formic acid was detected ($AgNO_3$ test). Hydrochloric acid was determined by the Volhard method. The distillate contained 1.816 g (79.8%) of HCl.

The aqueous solution was divided into two portions in one of which acetic acid was determined. To this portion was added freshly prepared Ag_2O. The precipitate of AgCl was filtered off and the solution containing the silver salts was evaporated to dryness. The crystalline residue was purified by recrystallization and dried in vacuo to constant weight; the mother liquors were evaporated to dryness in vacuo and the crystals which separated were again recrystallized. Analysis of the crystals showed that the silver salt composition corresponded to silver acetate; no other salts were found.

Found %: Ag 63.08. $C_2H_3O_2Ag$. Calculated %: Ag 64.58

In view of the absence of other acids it appeared possible to calculate the amount of acetic acid from the total acidity of the aqueous distillate. The total distillate required 5.6627 g KOH for neutralization, of which 2.7856 g was required to neutralize the hydrochloric acid, while 2.8771 g KOH was used up by the acetic acid which corresponds to 3.08 g (80%) of acetic acid. The second portion of the aqueous extract was treated with 10% sodium carbonate to weakly alkaline reaction, followed by extraction with ether. After removing the ether there was obtained 1.2 g of chloroacetone.

Found %: Cl 37.78. C_2H_5OCl. Calculated %: Cl 38.38.

Interaction with 2,4-dinitrophenylhydrazine gave orange crystals, m.p. 126 – 127°; literature, m.p. 124 – 125.5° [5].

Found %: Cl 12.83. $C_9H_9O_4N_4Cl$. Calculated %: Cl 13.92.

The content of chloroacetone in the extract was determined by reaction with hydroxylamine hydrochloride and was found to be 97.3%. From the amounts of CO_2 and chloroacetone obtained the yield of γ-chloroacetic acid was calculated to be 2.7613 g (83.6%).

Fraction No. 2 yielded 18.2 g of substance boiling at 105-107°/5 mm.

d^{20}_4 1.2824, $n^{20}D$ 1.508, MR_D 58.11; Calculated, 58.26.

Found %: Cl 56.09, Cl (ionizable) 28; M 245.9; 1 g of the substance absorbs 0.6373 g of bromine. $C_8H_{12}Cl_4F$. Calculated %: Cl 56.8, Cl (ionizable) 28.4. M 250; 1 g of the substance will absorb 0.6392 g Br_2.

9.25 g of the compound was taken for ozonolysis which was carried out in solution in chloroform. The reaction product was decomposed with a 3% hydrogen peroxide solution. After decomposition of the ozonide an oily product remained in the flask. The aqueous extract did not contain formic acid ($AgNO_3$ test). In order to determine any volatile acids the aqueous extract was distilled in vacuo (boiling point 60 – 62° at 160 mm). Hydrochloric acid was determined in the distillate (95.8 g) by titration (Volhard method). Content of HCl in

the solution, 1.2305 g (91%).

An aliquot portion of the aqueous solution was treated with freshly precipitated Ag_2O. The precipitate of AgCl which formed was filtered off. Silver acetate was isolated from the filtrate.

Found %: Ag 64.11. $C_2H_3O_2Ag$. Calculated %: Ag 64.58.

Since no other silver salts were found, apart from silver acetate, the yield of acetic acid was calculated from the total acidity of the mixture of the volatile acids. The aqueous solution required 3.55 g of KOH for neutralization of which 1.887 g was used to neutralize the HCl; consequently, 1.663 g was used to neutralize acetic acid which corresponds to 1.78 g (80.1%) of the acid.

The oily residue left after separation of the aqueous layer, was distilled in vacuo. After a second distillation there was obtained 5.04 g (62.9%) of β-chloromethyl-γ-dichlorovaleric acid, which is sparingly soluble in water but easily soluble in aqueous alcohol and acetone.

B.p. 113 – 115°/5.5 mm, d^{20}_4 1.3648, $n^{20}D$ 1.4975, MR_D 47.03; Calculated 46.88.

Found %: Cl 47.30. Equivalent Weight 258.4. $C_6H_9O_2Cl_3$. Calculated %: Cl 48.52. Equivalent Weight 255.1.

Fractionation of the products of polycondensation of 1,2-dichlorobutene-2. 65.1 g of the polymer was submitted to fractionation. Methanol was added portion-wise to the benzene solution of the polymer and the following fractions were separated: fraction 1, 9.5 g, (15.45%), fraction 2, 25.09 g (40.77%), fraction 3, 8.7 g (14.15%), fraction 4, 18.21 g (29.63%). The characteristics of the fractions are given in the table below.

Fraction No.	M (cryosc., in benzene)		Cl content (%)		Ionizable Cl (%)		Unsaturation (in g Br_2) per 1 g of substance		Molecular formula
	found	calc.	found	calc.	found	calc.	found	calc.	
1	1528.85	1541.0	40.38	41.54	2.137	2.33	1.725	1.765	$C_{68}H_{86}Cl_{18}$
2	888.4	921.18	42.28	42.37	3.827	3.85	1.712	1.736	$C_{40}H_{51}Cl_{11}$
3	381.18	390.5	45.078	45.43	9.28	9.11	1.608	1.64	$C_{16}H_{21}Cl_5$
4	264.2	—	—	—	—	—	—	—	Mixture of dimers and trimers

For ozonolysis we took 7.26 g of fraction 3. On decomposing the ozonide with water there was evolution of carbon dioxide (0.0032 g, absorbed in 1.0 N $Ba(OH)_2$). The products of decomposition contained resinous substance. Formic acid was absent. Hydrochloric and acetic acids were present. Hydrochloric acid was determined as chloride, and the fraction yielded 2.422 g of HCl. Acetic acid was determined as the silver salt.

Found %: Ag 64.12. $C_2H_3O_2Ag$. Calculated %: Ag 64.58.

A similar procedure was followed in the examination of the condensation products of 1,3-dichlorobutene-2 in the presence of the catalysts $AlCl_3$, $ZnCl_2$ and $SnCl_4$. The investigations have shown that by comparison with $FeCl_3$ as the catalyst, an increased yield of high molecular weight products is obtained in the presence of $AlCl_3$, while in the presence of $ZnCl_2$ the reaction proceeds at a slower rate.

SUMMARY

1. Polycondensation of 1,3-dichlorobutene-2 in the presence of Friedel – Crafts – Gustavson catalysts has been investigated.

2. The primary reaction product is the combination of two molecules of 1,3-dichlorobutene-2 giving 2,6,6-trichloro-5-chloromethylheptene-2; hydrogen chloride is then split off from the latter, giving 2,6-dichloro--5-chloromethylheptadiene-2,5.

3. In addition to the above compounds, polymers of higher molecular weights are also formed. The composition of these polymers confirms the mechanism of condensation proposed.

4. The authors have proposed a mechanism of vulcanization of polychloroprene in the presence of metal oxides through condensation under the influence of metal chlorides formed during the reaction.

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**In Russian.

INTERACTION OF 1,3-DICHLOROBUTENE-2 WITH CHLOROPRENE UNDER THE INFLUENCE OF FRIEDEL – CRAFTS – GUSTAVSON CATALYSTS. II.

A. L. Klebanskii, A. G. Saiadian and M. G. Barkhudarian

With the exception of α-haloesters [1-3], the addition of halogen derivatives to dienes has not been investigated sufficiently. The possibility of addition of tertiary butylene chloride and bromide as well as of crotyl chloride and bromide to divinyl has first been indicated in a patent [4]. Subsequently, A. A. Petrov and K. V. Leets [5] investigated the interaction of divinyl, isoprene and diisopropenyl with primary, secondary and tertiary halogen derivatives in the presence of zinc halides.

In conjunction with investigations which are being carried out by one of us on the synthesis of compounds simulating the fundamental structural types of synthetic rubbers, with a view to comparing their relative reactivities, we have undertaken a study of the interaction of crotyl chlorides of different structures with chloroprene, isoprene and divinyl.

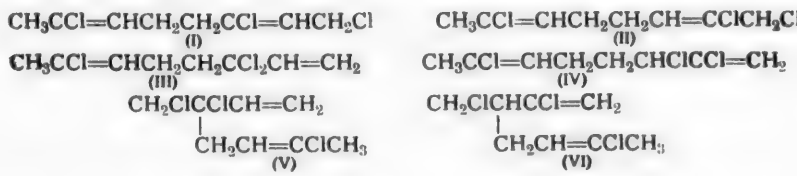
In the present paper we describe the results of our investigation of the interaction of 1,3-dichlorobutene-2 with chloroprene in the presence of catalysts, namely, $AlCl_3$ and $FeCl_3$. In both cases we have observed the formation of low molecular weight compounds as well as resinous products.

When $AlCl_3$ is used as the catalyst the yield of the adduct of one molecule of 1,3-dichlorobutene-2 to one molecule of chloroprene is very small, although the total amount of the various products of condensation is greater in this case. On increasing the catalyst concentration (to over 1 mole-%) there takes place preferential formation of high molecular weight compounds, which makes the isolation of the primary product of reaction difficult. The relative proportions of the reactants affects greatly the composition of the reaction products, the yield of the primary adduct increasing with increasing excess of 1,3-dichlorobutene-2.

In order to investigate the reaction mechanism we have isolated the primary reaction products.

As is well known, interaction of the catalyst with 1,3-dichlorobutene-2 gives rise to the formation of a complex (e.g. $CH_3CCl=CHCH_2^+ \cdot FeCl_4^-$) with a positively charged carbonium ion. The subsequent progress of the reaction depends on the interaction of this complex with chloroprene.

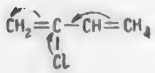
Addition of 1,3-dichlorobutene-2 to chloroprene may be expected to give rise to the formation of six different compounds as the primary products of the reaction:



The structure of the primary reaction products obtained was proved by ozonolysis. Among the products of decomposition we found acetic, chloroacetic and succinic acids in yields of 75.6%, 80.3% and 81.09%, respectively. From this it would follow that 1,3-dichlorobutene-2 adds on to chloroprene either in the 1,4 or

the 4,1 position (formulas I and II). Ozonolysis gives, however, no clue as to which of the two mechanisms is, in fact, operative, since in both cases acetic, chloroacetic and succinic acids are formed.

The most probable reaction mechanism may be established by a consideration of the distribution of electron density in the chloroprene molecule as depicted in formula (A).



(A)

This particular electron density distribution is confirmed by the mechanism of addition of HCl to chloroprene. This gives reasons to suppose that addition of the complex $CH_3CCl=CHCH_2^+ \cdot FeCl_4^-$ to chloroprene takes place in position 1,4.

In addition to compounds formed by the combination of one molecule of 1,3-dichlorobutene-2 and one molecule of chloroprene we have also isolated from the reaction products the adduct of 1,3-dichlorobutene-2 to two molecules of chloroprene. The composition of this adduct is expressed by the formula $C_{12}H_{16}Cl_4$. On the other hand, an adduct of two molecules of 1,3-dichlorobutene-2 to one molecule of chloroprene could not be detected among the products of the reaction.

The polymers were fractionated into narrow fractions by precipitation with methanol from benzene solution.

In the product of ozonolysis of the fraction having the composition $C_{20}H_{26}Cl_6$ we found acetic, chloroacetic and succinic acids. Analysis and ozonolysis show that this fraction is the condensation product of one molecule of 1,3-dichlorobutene-2 and four molecules of chloroprene.

We may, therefore, suppose that the interaction of 1,3-dichlorobutene-2 with chloroprene is a stepwise condensation: the primary product of the reaction is the adduct $CH_3CCl=CHCH_2CH_2CCl=CHCH_2Cl$, the next step being the formation of an adduct having the formula $CH_3CCl=CHCH_2(CH_2CCl=CHCH_2)_2Cl$, then $CH_3CCl=CHCH_2(CH_2CCl=CHCH_2)_3Cl$, and so on. Similar reactions have been described in the literature [6-8] and referred to as telomerization. Thus it appears that in the presence of 1,3-dichlorobutene-2 and under the influence of the catalysts $AlCl_3$ and $FeCl_3$, chloroprene undergoes a typical telomerization reaction.

EXPERIMENTAL

Interaction of 1,3-dichlorobutene-2 with chloroprene in the presence of ferric chloride. 62.5 g of 1,3-dichlorobutene-2 and 22.1 g of chloroprene and 1.285 g of $FeCl_3$ (1.0 mole-%) was kept in a sealed ampule, filled with nitrogen, at a temperature of 20° for 20 hours. In order to avoid further change of the reaction products during the subsequent treatment, the catalyst was removed by washing with 10% hydrochloric acid and water after which the residue was dried over $CaCl_2$. After removing the unreacted starting materials (13.1 g) the residue was fractionated in vacuo and the following fractions were collected: fraction 1, b.p. 95-110°/7 mm, 7.8 g; fraction 2, b.p. 130-150°/3 mm, 3.6 g; residue (polymer) 1.68 g. After a second distillation, fraction 1 yielded 4.2 g of substance with the following characteristics:

B.p. 101-103°/4.5 mm, d^{20}_4 1.2075, $n^{20}D$ 1.507, MR_D 52.64; Calculated 52.90.

Found %: Cl 49.50, ionizable Cl 16.02. M 206.55; bromine No. 147.2. $C_8H_{11}Cl_3$. Calculated %: Cl 49.88, ionizable Cl 16.68. M 213.5; bromine No. 149.7.

Ozonolysis was carried out with 8.55 g of the substance. After decomposition with water the resultant mixture of the acids did not contain any formic acid ($AgNO_3$ test). After removing the volatile acids in vacuo at 45-50° crystals of chloroacetic and succinic acids were left in the flask (6.87 g). The mixture of the volatile acids was found to contain 51.4% of the theoretical amount of HCl, as determined by determination of chloride by the Volhard method. An aliquot portion of the distillate was treated with freshly precipitated silver oxide. After separating the precipitate of silver chloride by filtration, the filtrate was evaporated in vacuo. The dry residue constituting the silver salt of the volatile acids was recrystallized and analysed.

Found %: Ag 63.92. $C_2H_3O_2Ag$. Calculated %: Ag 64.58.

Silver salts of other acids could not be detected. The amount of acetic acid was calculated from the total acidity of the mixed volatile acids. The distillate required total of 4.008 g KOH for neutralization, of which 2.31 g was used to neutralize the hydrochloric acid and 1.698 g KOH to neutralize acetic acid, which corresponds to 1.82 g (75.6%) of the latter acid.

From the crystalline residue there was obtained, by distillation, chloroacetic acid (b.p. 73-75° at 4.5 mm) in the form of white crystals melting at 61-62°. Literature, m.p. 61.5°.

Found %: Cl 37.02. Acid value 597. $C_2H_3O_2Cl$. Calculated %: Cl 37.57. Acid value 592.6.

The amount of chloroacetic acid obtained was calculated from the total chlorine content in the crystalline product (1.14 g), which corresponds to 3.04 g (80.3%) of chloroacetic acid.

The residual crystals of succinic acid (3.83 g, 81%) had a melting point of 180-181° after recrystallization. Literature, m.p. 182.3°.

Found: acid value 926.09. $C_4H_6O_4$. Calculated: 949.18.

After suitable treatment of fraction 3 there was obtained 1.5 g of a substance boiling at 140-142° at 3 mm.

Found %: Cl 46.81, ionizable Cl 11.25. M 289.5. $C_{12}H_{16}Cl_4$. Calculated %: Cl 47.02, ionizable Cl 11.76. M 302.

Interaction of 1,3-dichlorobutene-2 with chloroprene in the presence of aluminium chloride. Treatment of a mixture of 62.5 g of 1,3-dichlorobutene-2 and 22.1 g of chloroprene in the presence of $AlCl_3$ (1 mole-%) under conditions described above there was obtained, after removing the unreacted starting materials, 19.76 g of the reaction product of which 3.61 g distilled at 80-110°/4 mm, leaving a residue (polymer) amounting to 15.32 g.

From the distilled portion there was obtained a substance boiling at 101-103°/4.5 mm, d^{20}_4 1.2082, $n^{20}D$ 1.5686.

Found %: Cl 49.32, ionizable Cl 16.994. M 208.4; bromine No. 149.2. $C_8H_{11}Cl_3$. Calculated %: Cl 49.88, ionizable Cl 16.63. M 213.5; bromine No. 149.7.

Examination of the polymers. To the solution of the polymers in benzene was added, portion-wise, methanol; the fractions obtained are described in the table below.

Physicochemical Constants of Polymer Fractions

Fraction No.	Weight		Mean molecular weight (cryosc., in benzene)		Total chlorine (%)		Ionizable chlorine (%)		Calculated empirical formula
	g	%	found	calc.	found	calc.	found	calc.	
1	6.68	27.31	662.3	656.0	42.57	43.29	6.33	5.26	$C_{28}H_{36}Cl_8$
2	12.58	52.82	458.2	479.0	43.22	44.46	7.75	7.41	$C_{20}H_{26}Cl_6$
3	4.87	19.87	257.3	—	—	—	—	—	Mixture of dimers and trimers

7.82 g of fraction 2 was submitted to ozonolysis. The products of decomposition were examined as before. The mixture of the acids contained no formic acid ($AgNO_3$ test). After distillation of the volatile acids in vacuo at 30-40° the residue contained 6.92 g of a mixture of chloroacetic and succinic acid (with a small amount of tarry matter).

Hydrochloric acid was determined from the chloride content of the mixture of the volatile acids; the determination gave 2.23 g (74.33%) of HCl.

The presence of acetic acid was confirmed by precipitation of its silver salt.

Found %: Ag 63.24. $C_2H_3O_2Ag$. Calculated %: Ag 64.59.

Silver salts of other acids could not be found. The amount of acetic acid was calculated from the total acidity of the mixed volatile acids which required 4.114 g of KOH for neutralization; of this 3.421 g was taken up by hydrochloric acid and 0.693 g by acetic acid, which corresponds to 0.743 g (77.57%) of acetic acid.

Chloroacetic acid was isolated from the crystalline residue by distillation in vacuo, m.p. 59-61°.

Found %: Cl 36.92. Acid value 596. $C_2H_3O_2Cl$. Calculated %: Cl 37.57. Acid value 597.

Total chlorine content of the crystalline product was found to be 0.462 g, which corresponds to 1.23 g (80.38%) of chloroacetic acid.

After recrystallization the melting point of the succinic acid was 179-181°.

Found: Acid value 939.5. $C_4H_6O_4$. Calculated: Acid value 949.18.

The aqueous extract required 9.2 g of KOH for neutralization of which 3.243 g was used up by hydrochloric, acetic and chloroacetic acids. Therefore, 5.35 g* KOH was taken up by the succinic acid, which corresponds to 5.92 g (74.44%) of the acid.

SUMMARY

1. Interaction of 1,3-dichlorobutene-2 with chloroprene in the presence of $FeCl_3$ and $AlCl_3$ as catalysts has been investigated.

2. It has been shown that in the presence of either catalyst 1,3-dichlorobutene-2 adds on to chloroprene in the 1,4-position, with the formation of products containing one, two, three and more molecules of chloroprene.

3. The product of the interaction of one molecule of 1,3-dichlorobutene-2 with one molecule of chloroprene has the structure of 1,3,7-trichlorooctadiene-2,6.

4. The polymers formed result from the condensation of one molecule of 1,3-dichlorobutene-2 and several chloroprene molecules by a step-wise addition to the primary reaction product (telomerization).

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*As in original — Publisher's note.

**Original Russian pagination. See C.B. Translation.

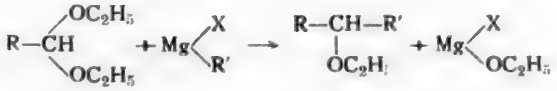
***In Russian.

INVESTIGATION OF THE EXCHANGE OF OXY-RADICALS WITH HYDROCARBON RADICALS OF ORGANOMAGNESIUM COMPOUNDS

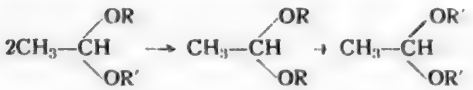
I. INVESTIGATION OF THE REACTIVITY OF MIXED ACETALS

M. F. Shostakovskii and M. R. Kulibekov

In order to investigate the reactivity of oxy-radicals of mixed acetals of the general formula $CH_3-CH(OAlk)(OR)$, where R = Alk, Ar is an alkaryl radical, we have made use of the Chichibabin-Elgazin reaction [1]. As is well known, these authors have established that symmetrical acetals react with Grignard reagents according to the scheme

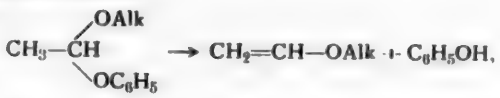


In the present investigation Grignard reagents were used to establish the lability of oxy-radicals in mixed acetals, a facet which has not so far been reported on in the literature. As regards the reactivity of mixed acetals it is well known that under the influence of mineral acids or heat they easily undergo symmetrization

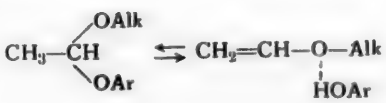


A characteristic reaction given by acetals, and one which demonstrates their high reactivity, is their interaction with simple vinyl ethers [2].

As regards the structure of mixed acetals it has been established from results of their thermal decomposition [3] in accordance with the scheme

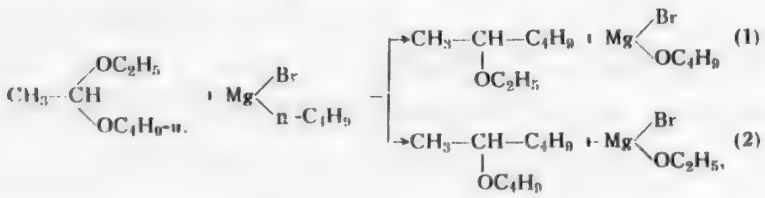


as also from investigation of their Raman spectra [4], that, for example, mixed alkaryl acetals may exist in the following two forms



In view of the fact that mixed acetals are assuming increasing theoretical and practical importance we have decided to investigate in detail the lability of their oxy-radicals by interaction with Grignard reagents. Three groups of mixed acetals were included in this investigation: (1) dialkyl, (2) alkyl-aryl and (3) alkyl-alkaryl acetals.

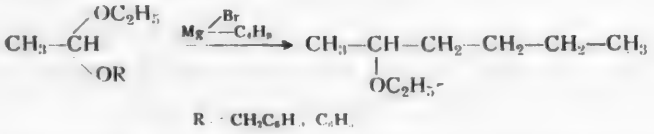
In the course of the investigation of the interaction of ethylbutyl acetal with butyl magnesium bromide it has been found that the reaction proceeds in two directions:



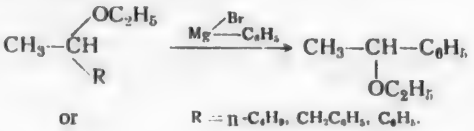
of which reaction (1) is the predominant one.

On acting on the same acetal with ethyl magnesium bromide it was found that neither the ethoxy nor the butoxy group undergoes substitution. Under the conditions of the reaction symmetrization of ethylbutyl acetal to the corresponding symmetrical acetals takes place. An analogous reaction with ethylbenzyl acetal also gave a negative result. Under the conditions of the reaction a portion of the ethylbenzyl acetal remains unchanged while a certain amount undergoes symmetrization with the formation of dibenzyl acetal. It may be concluded from this that under the conditions of the reaction ethyl bromide, unlike other alkyl (aryl) halides, favors symmetrization of mixed acetals.

On acting on ethylbenzyl and ethylphenyl acetals with butyl magnesium bromide, the ethyl ether of hexanol-2 is the sole product of the reaction.

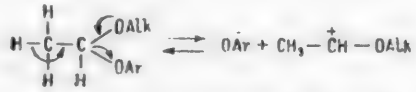


Action of phenyl magnesium bromide on ethylbutyl, ethylbenzyl and ethylphenyl acetals again gives one and the same ether as the main reaction product.



The formation of ethylethers of hexanol-2 and of secondary phenylethyl alcohol shows unequivocally that in mixed acetals the butyl and phenyl radicals displace the larger oxy-radicals, the displacement being particularly easy with ethylphenyl acetal.

On the basis of these investigations we are lead to the conclusion that the lability for reactivity of given oxy-radicals of mixed acetals is determined by their electronic structure which facilitates the release of the OAr group in the form of an anion [5], with the formation of a carbonium ion;



The latter is easily stabilized either according to the scheme: $CH_3-\overset{+}{C}H-OAlk \rightarrow \overset{+}{H} + CH_2=CH-OAlk$ or the scheme $CH_3 \rightarrow \overset{+}{C}HOAlk + R \rightarrow \underset{\displaystyle R}{CH_3CHOAlk}$, where R = Alk, Ar or an alkaryl radical which determines the course of the exchange reaction.

EXPERIMENTAL

1. Interaction of ethylbutyl acetal with butyl magnesium bromide. Into a round-bottomed flask, provided with a stopcock, a mechanical stirrer, air-condenser and a dropping funnel, was placed 45 g of ethylbutyl acetal [b.p. 144-146° (735 mm), $n^{19}D$ 1.3995]. After heating up the contents on a boiling water bath an ether solution of butyl magnesium bromide, prepared in the usual way from 8 g of magnesium and 40 g of butyl bromide, was added slowly dropwise. As the reaction proceeded the solvent was gradually removed from the reacting system. When all of the organo-magnesium compound had been added heating was continued for 2-3 hours, the solvent being continuously removed. The reaction mixture was observed to heat up spontaneously (spontaneous boiling). At the end of the reaction time the reaction product was decomposed with water and 2-5% acetic acid. Whenever no unreacted organo-magnesium compound was present the decomposition with water proceeded slowly, without any excessive evolution of heat. The upper layer containing the required product was separated from the aqueous layer and was washed with 10% hydrochloric acid in order to hydrolize the unreacted acetal. The product obtained was then dissolved in ether, followed by washing with a weak sodium carbonate solution, and water, and was then dried over Na_2SO_4. The ether was removed on a water bath, the residue was fractionated at normal pressure.

The following fractions were collected:

Fraction 1- 101-123°, 1.5 g; fraction 2- 124-126°, 8 g, $n^{20}D$ 1.3964, d^{20}_4 0.7700, MR_D 40.60; Calculated 40.79; fraction 3-127-167°, 1 g; fraction 4- 168-170°, 3 g, $n^{20}D$ 1.4098, d^{20}_4 0.7874, MR_D 50.13; Calculated 50.02. Residue 2 g.

The fraction boiling at 124-126° (747 mm) was identified as the ethyl ether of hexanol-2.

Found %: C 73.81; 73.94; H 13.80, 13.90. $C_8H_{18}O$. Calculated %: C 73.84; H 13.84.

The ethyl ether of hexanol-2 is a mobile clear colorless liquid having the odor of fruit. It is insoluble in water, but dissolves easily in organic solvents.

The fraction boiling at 168-170° (747 mm) was identified as the butyl ether of hexanol-2.

Found %: C 76.73, 73.68; H 14.00, 14.08. $C_{10}H_{22}O$. Calculated %: C 76.94; H 13.92.

The butyl ether of hexanol-2 is a colorless clear liquid with an aromatic odor. It is insoluble in water but dissolves easily in many organic solvents.

2. Interaction of ethylbutyl acetal with ethyl magnesium bromide. Under conditions similar to those used in the foregoing experiment ethyl magnesium bromide prepared from 6 g of magnesium and 27 g of ethyl bromide was added to 18 g of ethylbutyl acetal. Decomposition of the colorless reaction product with water was accompanied by vigorous fuming (after each drop of water) and spontaneous heating of the reaction mixture and for this reason the decomposition was conducted with external cooling. After suitable purification the product was distilled at atmospheric pressure.

The following fractions were collected: fraction 1, 99-179°, 2.5 g, $n^{21}D$ 1.4008; fraction 2, 179-181°, 4 g, $n^{21}D$ 1.4065. Residue 1.5 g.

Both fractions were combined and distilled again over metallic sodium. There was obtained 4 g of a liquid boiling at 182-183° (754.5 mm), $n^{20}D$ 1.4075, d^{20}_4 0.8277, which was identified as dibutyl acetal.

3. Interaction of ethylbutyl acetal with phenyl magnesium bromide. The preparation was carried out with 3 g of magnesium, 19 g of bromobenzene and 15 g of ethylbutyl acetal under conditions similar to those described in the foregoing experiments. The crude reaction product was of a dark brown color. No strong evolution of heat was observed during decomposition of the product with water. After suitable treatment the product was distilled in vacuo.

The following fractions were collected: fraction 1, 76-84° (10 mm), 3 g; fraction 2, 85-102° (10 mm), 5 g; residue 1 g.

Both fractions were combined and redistilled over metallic sodium. There was obtained 4.5 g of a liquid boiling at 120-122° (35 mm), $n^{20}D$ 1.4910, d^{20}_4 0.9203, which corresponds to the ethyl ether of sec. phenylethyl alcohol. Literature [6] gives a boiling point of 185-187°, d^{21} 0.931.

4. Interaction of ethylphenyl acetal with butyl magnesium bromide. Butyl magnesium bromide was prepared from 8 g of magnesium and 52 g of butyl bromide. Under conditions described above this reagent was added to 50 g of the acetal. After the addition of the first few drops a considerable amount of phenol separated and the reaction mixture turned into a solid black mass. The reaction product was extracted with ether and treated in the usual way. After removing the ether the residual mass became more and more viscous and finally changed into a dark-brown resin, resembling varnish rosin, which may have some practical application. The formation of the resin may be explained as being due to the decomposition of the acetal to vinylethyl ether and phenol under the action of the Grignard reagent under the given experimental conditions. The vinylethyl ether undergoes polymerization, the process being possibly catalyzed by the Grignard reagent. In order to prevent formation of the resin we changed the experimental conditions. To the prepared butyl magnesium bromide was added dropwise ethylphenyl acetal (without heating). After a short time the reaction mixture heated up spontaneously and came to the boil necessitating cooling with water. The product was decomposed with water without any marked evolution of heat. After the usual treatment the product was then distilled at atmospheric pressure.

The following fractions were collected: fraction 1, 80-126°, 2 g, $n^{20}D$ 1.3980, d^{20}_4 0.7927; fraction 2, 127-130°, 6 g, $n^{20}D$ 1.3970, d^{20}_4 0.7732; fraction 3, 131-132°, 5 g, $n^{20}D$ 1.3976; d^{20}_4 0.7730. Residue 1.5 g.

Fractions 2 and 3 were combined and redistilled over metallic sodium yielding 8 g of the ethyl ether of hexanol-2: b.p. 126-128° (741.5 mm), $n^{20}D$ 1.3952, d^{20}_4 0.7670, MR_D 40.65; Calculated 40.79.

5. Interaction of ethylphenyl acetal with phenyl magnesium bromide. To phenyl magnesium bromide prepared from 3 g of magnesium and 19 g of bromobenzene was added, dropwise, 16 g of the acetal [b.p. 87.5-88.5° (11 mm), $n^{19}D$ 1.4972]. The synthesis was carried out under the same conditions as those described above. The reaction product was distilled in vacuo. The fraction boiling at 75-76° (12 mm) was collected (10.7 g). In the later stages of the distillation phenol crystallized in the condenser. The fraction boiling at 75-76° (12 mm) was redistilled twice over metallic sodium. There was obtained 5 g of a liquid boiling at 70.5° (12 mm), $n^{20}D$ 1.4930, d^{20}_4 0.9220, MR_D 47.28; Calculated 46.42.

This liquid was identified as the ethyl ether of sec. phenylethyl alcohol. Its structure was proved by synthesis of the analogous acetal from ethylbutyl acetal and phenyl magnesium bromide (Experiment No. 3).

6. Interaction of ethylbenzyl acetal with ethyl magnesium bromide. Ethyl magnesium bromide was prepared from 6 g of magnesium turnings and 27 g of ethylbromide. The reagent was added from a dropping funnel to 32 g of ethylbenzyl acetal, as in Experiment No. 1. On decomposing the product with water there was copious evolution of fumes and spontaneous heating of the reaction mixture. The product was distilled over metallic sodium.

Fractions collected: Fraction 1, b.p. 102-103° (10 mm), 7 g, $n^{19}D$ 1.4878; d^{19}_4 0.9777; fraction 2, 182-183° (10 mm), 7 g, $n^{19}D$ 1.5388, d^{19}_4 0.0491. Residue 1.5 g.

Fraction No. 1 was found to be ethylbenzyl acetal and fraction 2 was identified as dibenzyl acetal; this result indicates that no symmetrization takes place. On the other hand ethylbenzyl acetal undergoes symmetrization under the action of ethyl magnesium bromide.

The ethylbenzyl acetal used in this synthesis was first prepared by us in 70% yield by the method described previously [8].

B.p. 219-220°, $n^{20}D$ 1.4861, d^{20}_4 0.9783, MR_D 52.83; Calculated 52.68.

Found %: C 73.70, 73.70; H 8.88, 8.94. $C_{11}H_{16}O_2$. Calculated %: C 73.33; H 8.88.

Ethylbenzyl acetal is a clear colorless liquid with a light odor of ether. It is insoluble in water.

7. Interaction of ethylbenzyl acetal with butyl magnesium bromide. The preparation was carried out with 6 g of magnesium, 34 g of butyl bromide and 40 g of the acetal under the same conditions as in Experiment No. 1. The reaction product was distilled at atmospheric pressure.

Obtained: fraction 1, b.p. 102-122°, 0.5 g; fraction 2, 123-126°, 2.5 g; fraction 3, 127-129°, 4 g. Residue 7 g.

Fractions 2 and 3 were combined and redistilled over metallic sodium. There was obtained 3.5 g of the ethyl ether of hexanol-2, b.p. 129-130.5° (754 mm), $n^{20}D$ 1.3990, d^{20}_4 0.7681. The 7 g of the residue was

identified as a benzyl alcohol. The structure of the product follows from the synthesis described in the foregoing experiments (Experiment Nos. 1, 4, 7).

8. Interaction of ethylbenzyl acetal with phenyl magnesium bromide. The preparation was carried out with 1/8 mole of each reagent, the conditions being similar to those in Experiment No. 1. The resultant product was distilled in vacuo, yielding 5.5 g of a liquid [b.p. 75-77° (14 mm), $n^{20}D$ 1.4945, d^{20}_4 0.9233], which was identified as the ethyl ether of sec. phenylethyl alcohol [6].

9. Interaction of butyl benzyl acetal with phenyl magnesium bromide. The Grignard reagent was prepared from 8 g of magnesium and 50 g of bromobenzene. It was added to 55 g of butylbenzyl acetal preheated on a water bath. The reaction product was fractionated in vacuo.

Fractions obtained: Fraction 1, 92.5-93.5° (13 mm), 9 g, $n^{20}D$ 1.5040, d^{20}_4 0.9626; fraction 2, 94-99° (13 mm), 5 g, $n^{20}D$ 1.4930, d^{20}_4 0.9333. Residue 2 g.

The two fractions were combined and treated with metallic sodium. A vigorous reaction took place with the formation of a fluffy precipitate. The reaction product was separated from the precipitate by filtration and distilled over metallic sodium. The following fractions were collected: Fraction 1, 214-218° (758 mm), 2 g, $n^{20}D$ 1.4862, d^{20}_4 0.9133; fraction 2, 219-220° (758 mm), 3.5 g, $n^{20}D$ 1.4848, d^{20}_4 0.9105.

The fraction boiling at 219-220.5° (758 mm), was identified as the butyl ether of sec. phenylethyl alcohol. Literature [7] gives a boiling point of 220-222° (730 mm), d^{20}_4 0.9063, $n^{20}D$ 0.4832.

The butylbenzyl acetal used in this preparation was first obtained by us in approximately 75% yield by the method described previously [8]. The acetal has the following characteristics:

B.p. 142.5° (18 mm), d^{20}_4 0.9530, $n^{20}D$ 1.4794, MR_D 61.59; Calculated 61.92.

Found %: C 74.70, 74.59; H 9.44, 9.28. $C_{13}H_{20}O_2$. Calculated %: C 75.00; H 9.61.

Butylbenzyl acetal is a clear colorless liquid with a faint odor of ether. It is insoluble in water but dissolves easily in many organic solvents.

SUMMARY

1. The exchange of oxy-radicals of mixed acetals for alkyl and aryl radicals of Grignard reagents has been investigated.

2. It has been shown that it is the heavier oxy-radicals which undergo displacement.

3. The synthesis of the ethyl and the butyl ethers of hexanol-2, ethylbenzyl acetal and butylbenzyl acetal has been described for the first time.

The high reactivity of alkyl-aryl acetals has been demonstrated.

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ELECTRON CHARGE DENSITY OF CHEMICAL BONDS AND THE CHEMICAL PROPERTIES OF MOLECULES

I. ENERGIES OF ACTIVATION OF SUBSTITUTION REACTIONS AT A SATURATED CARBON ATOM

G. V. Bykov

In earlier papers we have shown [1-3] that the magnitude of the electron charge density of a covalent bond determines its more important physical characteristics and its behavior in chemical reactions. There is thus opened the possibility of a broad interpretation of chemical properties of complex molecules based, firstly, on the introduction of a new structural factor, namely, the electron charge density of the bond, and, secondly, on the fact that the regularities observed in chemical properties follow from the already established relationships between electron charge densities and energy parameters of molecules and individual bonds. A particular feature of the treatment of the problem outlined here is its semiquantitative character; however, in order to deduce qualitative relationships relating to the reactivity of molecules it is sufficient to know not the absolute, but merely the relative values of electronic charges of the bonds involved. The author has already put forward and exemplified [3] the following hypothesis: the energy of activation and hence, also the rate of substitution at a given bond are related to its electron charge density. In the present communication we shall apply this hypothesis to substitution reactions at a saturated carbon atom by different mechanisms. Corresponding reactions with unsaturated and aromatic compounds will be dealt with later. The discussion which follows will therefore apply to σ-electron bond charges only.

Electrophilic (a), radical (b) and nucleophilic (c) substitution reactions following a unimolecular mechanism may be represented by the following schemes:

$$R-|X \rightarrow R^- + X^+ \quad \text{followed by} \quad R^- + Y^+ \rightarrow R-Y \ (a)$$
$$R \dot{+} X \rightarrow R\cdot + X\cdot \quad \text{followed by} \quad R\cdot + Y\cdot \rightarrow R-Y \ (b)$$
$$R|-X \rightarrow R^+ + X^- \quad \text{followed by} \quad R^+ + Y^- \rightarrow R-Y \ (c)$$

The rate of these reactions is determined by the rate of the slowest step — the breakdown of the molecule R — X into R and X. It is evident that the energy of activation of this step will be less, and the rate of reaction greater,* in case (a) the smaller the electron charge of the R — X bond. The same holds true in case (c) the greater the charge of the R — X bond. Less clear is the situation in case (b), but since the energies of radical dissociation of bonds are, in general, symbatic to the "mean" bond energies which, in turn, are proportional to the bond electron charges [1], it may be assumed that the energy of activation of the radical substitution reaction will be less the smaller the electron charge density of the corresponding bond. As will be seen later, this assumption does, in fact, correspond to reality.

When the above-mentioned reactions proceed according to the bimolecular mechanism they involve the formation of the intermediate complex $Y \ldots . \overset{|}{\underset{\wedge}{C}} \ldots . X$. The energy of activation of such reactions is

* In comparing different reactions involving similar reagents, reaction mechanisms and experimental conditions, we may neglect the changes (as we pass from one reaction to another) in the pre-exponential term in Arrhenius' equation and compare only the energies of activation of the reactions or the rate constants which are simply related to the former.

made up mainly of two components: the energy of repulsion between Y and the carbon atom together with the original atoms attached to it, and the energy required to stretch the C – X bond, which, in turn, depends on the electron charge density of this bond. If in a series of different molecules the carbon atoms at which substitution is to take place do not differ to any great extent with respect to electronegative character from the atoms attached to them, then the differences in the energies of activation between the individual reactions will be mainly due to differences in the electron charge density of the C – X bonds in the various molecules. What has been said above with regard to the role of the electron charge density in substitution reactions by the unimolecular mechanism applies again in this case.

We shall now carry out a comparison of the energies of activation of substitution reactions with the electron charge densities of the corresponding bonds. A simple formula has been proposed [1,4] for calculating the electron charge density of a bond, A_{CX}:

$$A_{CX} = 1 + \frac{4E_X}{\Sigma E},$$

where E_X is the electronegativity of the monovalent atom X and ΣE the sum of electronegativities of all the atoms attached to the carbon atom forming the C – X bond. In applying this formula we shall make use of the electronegativity scale referred to hydrogen, as put forward by B. V. Nekrasov [5]:

H	Li	C	Cl	Br	I
1.00	0.40	1.19	1.43	1.37	1.24

The substitution of lithium by hydrogen in organolithium compounds is a characteristic example of electrophilic substitution. In the formation of the lithium derivative of dibenzofuran:

$$R - Li + C_{12}H_8O \rightarrow R - H + C_{12}H_7LiO$$

the ease of demetalation of lithium alkyls decreases [6] and, consequently, the energy of activation, ε, of the metallation reaction increases in the series:

$$\underset{A_{CLi}=1.40}{(CH_3)_3CLi} < \underset{1.42}{CH_3CHLiCH_2CH_3} < \underset{1.45}{CH_3CH_2CH_2CH_2Li} < \underset{1.47}{CH_3Li} \text{ electrons}$$

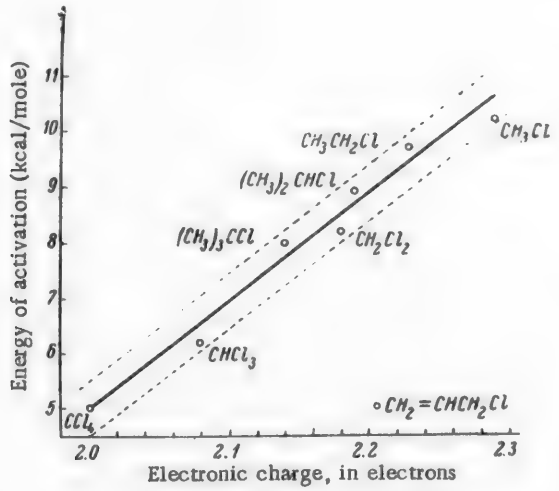

Fig. 1. Dependence of the energy of activation of the reaction $Na^{\cdot} + RCl \rightarrow NaCl + R^{\cdot}$ [8,9] on σ-electron charge density of the C – Cl bond.

a feature which runs parallel to the increasing σ-electron charge of the C – Li bonds. The inequality signs in this case again refer to the energies of activation of the corresponding reactions.

In radical substitution, for example in the case of the nitration of unsaturated hydrocarbons, the ease of substitution of hydrogen becomes less and the energy of activation, ϵ, greater in the series:

$$\begin{matrix} & R_3CH & < & R_2CH_2 & < & RCH_3 \\ A_{CH} = & 1.88 & & 1.91 & & 1.95 \text{ electrons} \end{matrix}$$

M. B. Neiman and co-workers [7] have found that in isotope exchange reactions $R\dot{I} + I \cdot \rightarrow RI + \dot{I} \cdot$, which take place in cyclohexane solutions of active alkyl iodide and inactive free iodine (which gives rise to the formation of atomic iodine under the influence of light) the following relationship between the energies of activation holds:

$$\begin{cases} \epsilon \text{ for } & CHI_3 & < & CH_2I_2 & < & CH_3I \\ A_{CI} = & 2.05 & & 2.11 & & 2.17 \text{ electrons} \end{cases}$$

$$\begin{cases} \epsilon \text{ for } & (CH_3)_2CHI & < & CH_3CH_2I & < & CH_3I \\ A_{CI} = & 2.07 & & 2.12 & & 2.17 \text{ electrons} \end{cases}$$

We thus find that there is a definite parallelism between the decrease in the rate of reaction, the increase in the energy of activation of the reaction, and the increase in the electron charge density of the bond involved in a substitution reaction by the radical mechanism. From Fig. 1 it will be seen that there is a linear relationship between the energies of activation of the reaction $Na \cdot + RCl \rightarrow NaCl + R \cdot$ and the electron charge density of the C – Cl bond being ruptured. At any rate, all the points, with the exception of one, come to lie within a band bounded by two parallel broken lines which correspond to the limits of error in the determination of the energy of activation of the reaction in question, namely, ± 0.5 kcal/mole (according to Semenov [8] the limits of error in such determinations are, at best, ±0.5-1.0 kcal/mole). The point representing the case of allyl chloride lies well outside this band; however, the problem of the special features of the "allylic position" of the substituent belongs to the class of unsaturated compounds which is not being touched upon here.

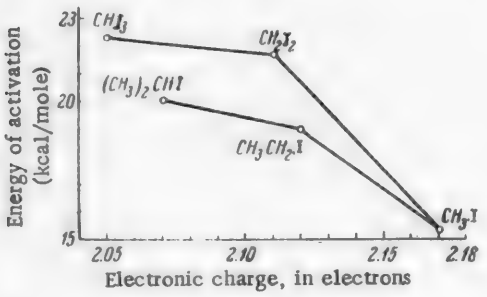

Fig. 2. Dependence of the energy of activation of the reaction $R\dot{I} + I \rightarrow RI + \dot{I}^-$ on σ-electronic charged density of the C – I bond.

Neiman and co-workers have also investigated [7] the nucleophilic substitution-reactions $RX + \dot{X}^- \rightarrow R\dot{X} + X^-$, where X = Br or I. They effected the interaction between the inactive alkyl halide and an active sodium halide, in solution in aqueous alcohol. It is found that the relationship between the rate of reaction and the energy of activation, on the one hand, and the electron charge densities of the C – X bonds, on the other, is the reverse of what has been observed in the case of substitution by the radical mechanism. Thus,

$$\begin{cases} \epsilon \text{ for } & CH_3Br & < & CH_2Br_2 & < & CHBr_3 \\ A_{CBr} = & 2.25 & & 2.16 & & 2.07 \text{ electrons} \end{cases}$$

$$\begin{cases} \epsilon \text{ for } & CH_3Br & < & CH_3CH_2Br & < & (CH_3)_2CHBr \\ A_{CBr} = & 2.25 & & 2.20 & & 2.15 \text{ electrons} \end{cases}$$

$$\begin{cases} \epsilon \text{ for } & CH_3Br & < & CH_3CH_2Br & < & CH_3CH_2CH_2Br \\ A_{CBr} = & 2.25 & & 2.20 & & \text{less than } 2.20 \text{ electrons} \end{cases}$$

With regard to the last series it must be noted that in accordance with a hypothesis formulated earlier [1] (i.e. of several atoms of one and the same element greater electronegativity will be exhibited by that atom which is directly attached to more electronegative atoms). The carbon atom in the methylene group should exhibit somewhat greater electronegativity than the carbon atom of a methyl group, and consequently, the electron charge density of the C – Br bond in n-propyl bromide should be somewhat smaller than in ethyl bromide. From this it follows that in nucleophilic substitution reactions ethyl bromide should be more active than n-propyl bromide.

The comparison of energies of activation determined by Neiman for reactions involving nucleophilic substitution reactions with alkyl iodides is illustrated graphically in Fig. 2. For similar values of electron charge densities of the C – I bonds the energies of activation are smaller for those derivatives of methyl iodide which have been obtained by substituting its hydrogen atoms by methyl groups, whereas they are greater when these atoms are substituted by further iodine atoms. This result is explained by the fact that in the latter case the component of the energy of activation necessary to overcome the force of repulsion between the entering

substituent and the group of atoms surrounding the carbon atom to be substituted is greater in the latter case (cf. [3]).

The examples of substitution reactions at a saturated carbon atom considered here are, of course, relatively simple since here we have to take into account only the distribution of σ-electron charges in the molecule. However, even in cases of substitution in the "allylic position" the distribution of the π-electronic cloud among the bonds of the molecule begins to exert an influence on the energy of activation of such reactions. Only when methods are developed which permit the calculation, or even a rough estimation, of the distribution of electron charge densities in unsaturated compounds, including aromatic ones, will be possible to investigate the dependence of the energy of activation of reactions on the distribution not only of σ-, but also of π-electronic charges.

SUMMARY

1. The energy of activation of electrophilic and radical substitution reactions at a saturated carbon atom increases with increasing σ-electronic charge density of the bond involved in the substitution.

2. The reverse type of dependence governs nucleophilic substitution.

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DOUBLE DIAZONIUM SALTS OF METHYLTIN TRICHLORIDE AND DIETHYLTIN DICHLORIDE

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The well-known double diazonium salts of tin tetrachloride have first been synthesised by Griess [1] and have later been investigated in detail by Kocheshkov and Nesmeianov [2]. These salts are the starting materials in the preparation of organotin compounds by the diazo method developed by Nesmeianov [3]. As regards double diazonium salts of organotin compounds, these have so far been unknown. The present paper describes the preparation of double diazonium salts of methyltin trichloride and diethyltin dichloride.

One of us [4] has developed a method for the synthesis of double diazonium salts of organoantimony compounds based on an exchange reaction between the double diazonium salt of ferrous chloride and the given organoantimony compound. This method was also found applicable in the preparation of double diazonium salts of methyltin trichloride. These salts were precipitated on mixing, in the cold, in an acetone solution of the freshly prepared diazonium salt* $ArN_2Cl \cdot FeCl_3$ with a methanolic solution of CH_3SnOOH saturated with hydrogen chloride. The reactions which take place may be expressed by the following equations.

$$CH_3SnOOH + 3HCl \rightarrow CH_3SnCl_3 + 2H_2O,$$

$$2ArN_2Cl \cdot FeCl_3 + CH_3SnCl_3 \rightarrow (ArN_2Cl)_2 \cdot CH_3SnCl_3 + 2FeCl_3.$$

The salts $(C_6H_5N_2Cl)_2 \cdot CH_3SnCl_3$ and $(p\text{-}C_7H_7N_2Cl)_2 \cdot CH_3SnCl_3$ could not be prepared by this method since on mixing the solutions in the cold vigorous evolution of nitrogen took place. The double salts $(p\text{-}O_2NC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$ and $(m\text{-}O_2NC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$ were precipitated only in traces, evidently because of their good solubility.

Subsequently we have worked out a simpler single-step method of synthesis of double diazonium salts of methyltin trichloride.** A solution of CH_3SnOOH in hydrochloric acid was added to the diazonium solution prepared by diazotizing the aromatic amine in hydrochloric acid with solid sodium nitrite; a precipitate of the salt $(ArN_2Cl)_2 \cdot CH_3SnCl_3$ formed at once. When it was attempted to prepare in this way the double salt using o-toluidine there was evolution of nitrogen and the salt did not precipitate. The double salts formed with $p\text{-}O_2NC_6H_4N_2Cl$ and $p\text{-}CH_3COC_6H_4N_2Cl$ did not precipitate probably because of their solubility in hydrochloric acid. It must be noted that the double salt does form with phenyl diazonium chloride, but in spite of many attempts could not be obtained in the pure state. Double diazonium salts of methyltin trichloride prepared by both methods are listed in Table 1.

The single-step method of preparation of double diazonium salts in hydrochloric acid solution which was found best for the purpose of the synthesis of salts of the type $(ArN_2Cl)_2 \cdot CH_3SnCl_3$, could not be applied to the preparation of double diazonium salts of diethyltin dichloride in view of the poor solubility of the latter in hydrochloric acid. On the other hand, on mixing the hydrochloric acid solution of the aryldiazonium chloride with an alcoholic solution of diethyltin dichloride gives rise to the co-precipitation of sodium nitrite which is formed during diazotization. For this reason we have adopted the following method to prepare double

* Double diazonium salts of ferrous chloride were prepared by the method described in [2].

** Double diazonium salts with $p\text{-}BrC_6H_4N_2Cl$ and $C_6H_5N_2Cl$ were also prepared by mixing an alcoholic solution of ArN_2Cl with an alcoholic solution of CH_3SnOOH saturated with hydrogen chloride.

TABLE 1

Double diazonium salt	Melting point (decomp.)	Yield (%) Method I	Yield (%) Method II
$(p\text{-}CH_3C_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$ . .	112°	34.0	34.0
$(p\text{-}CH_3OC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$.	165	32.5	42.0
$(p\text{-}BrC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$ . . .	147	—	42.5
$(p\text{-}C_2H_5OCOC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$	108	25.0	25.0
$(o\text{-}O_2NC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$ . .	106	—	43.7

diazonium salts of $(C_2H_5)_2SnCl_2$:•• the amine hydrochloride was dissolved in alcohol and diazotized with isoamyl nitrite and to the diazo solution was then added an alcoholic solution of diethyltin dichloride. The formation of the double salt of $(C_2H_5)_2SnCl_2$ may be expressed by the following equations:

$$ArNH_2 \cdot HCl + C_5H_{11}ONO \rightarrow ArN_2Cl + C_5H_{11}OH + H_2O,$$
$$2ArN_2Cl + (C_2H_5)_2SnCl_2 \rightarrow (ArN_2Cl)_2 \cdot (C_2H_5)_2SnCl_2.$$

The salts prepared by this method are listed in Table 2. Attempts to synthesise by this method the double diazonium salts starting from $p\text{-}O_2NC_6H_4NH_2$ and $p\text{-}CH_3COC_6H_4NH_2$ were unsuccessful because of the good solubility of these salts in alcohol.

TABLE 2

Double diazonium salts	Melting point (decomp.)	Yield (%)
$(C_6H_5N_2Cl)_2 \cdot (C_2H_5)_2SnCl_2$	80—81°	94
$(p\text{-}CH_3C_6H_4N_2Cl)_2 \cdot (C_2H_5)_2SnCl_2$ . .	88—89	74
$(p\text{-}ClC_6H_4N_2Cl)_2 \cdot (C_2H_5)_2SnCl_2$ . . .	98—99	83
$(p\text{-}BrC_6H_4N_2Cl)_2 \cdot (C_2H_5)_2SnCl_2$ . . .	110	68
$(p\text{-}C_2H_5OCOC_6H_4N_2Cl)_2 \cdot (C_2H_5)_2SnCl_2$	80	85

Double diazonium salts of methyltin trichloride and diethyltin dichloride have, as have the corresponding salts of $SnCl_4$, a constant composition $[ArN_2]_2^+[CH_3SnCl_5]^{--}$ or $[ArN_2]_2^+[(C_2H_5)_2SnCl_4]^{--}$ which is independent of the amounts of reagents used or of the character of the aryl radicals of the diazonium compound. Salts of both types are colorless crystalline compounds which undergo change on exposure to light, are easily soluble in water, less soluble in alcohol, and insoluble in ether, acetone and benzene.

EXPERIMENTAL

Preparation of double diazonium salts of CH_3SnCl_3 by mixing hydrochloric acid solutions of ArN_2Cl and CH_3SnCl_3. 1. 1.93 g (0.018 mole) of $p\text{-}CH_3C_6H_4NH_2$ was diazotized with 1.2 g (0.018 mole) of $NaNO_2$ in a mixture of 5.4 ml of conc. HCl and 5.4 g of ice. To the diazo solution was added a cold solution of 1.5 g (0.009 mole) of CH_3SnOOH in 10 ml of conc. HCl. The precipitated double salt was filtered off and purified by reprecipitation from methanol with ether. Yield 1.6 g (34%). M.p. 112° (decomp.)

• Preparation of the double salts $(ArN_2Cl)_2 \cdot CH_3SnCl_3$ by method I involved the formation of double diazonium salts of ferrous chloride; preparation by method II was by mixing solutions of ArN_2Cl in hydrochloric acid with CH_3SnOOH.

•• The reaction between $ArN_2Cl \cdot FeCl_3$ with diethyltin dichloride to yield double diazonium salts of diethyltin dichloride was not investigated.

Found %: N 10.35, 10.19; Sn 21.72, 21.97.* $(C_7H_7N_2Cl)_2 \cdot CH_3SnCl_3$. Calculated %: N 10.20; Sn 21.61.

2. From 2.2 g (0.018 mole) of p-$CH_3OC_6H_4NH_2$ and 1.5 g (0.009 mole) of CH_3SnOOH there was obtained, under conditions described in the foregoing experiment, 2.2 g (42%) of the corresponding double diazonium salt. M.p. 164-165° (decomp.).

Found %: N 9.13, 9.15. $(CH_3OC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$. Calculated %: N 9.63

3. From 3.1 g (0.018 mole) of p-$BrC_6H_4NH_2$ and 1.5 g (0.009 mole) of CH_3SnOOH was obtained 2.6 g (42.2%) of the double diazonium salt under the usual conditions; M.p. 147° (decomp.).

Found %: N 8.70, 8.89; Sn 17.99, 17.65 $(p\text{-}BrC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$. Calculated %: N 8.89; Sn 17.48.

4. From 3 g (0.018 mole) of p-$C_2H_5OCOC_6H_4NH_2$ and 1.5 g (0.009 mole) of CH_3SnOOH there was obtained 1.5 g (25%) of the double diazonium salt; M.p. 108° (decomp.).

Found %: Sn 17.72, 17.78. $(C_2H_5OCOC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$. Calculated %: Sn 17.84.

5. From 2.5 g (0.018 mole) of o-$O_2NC_6H_4NH_2$ and 1.5 g (0.009 mole) of CH_3SnOOH there was obtained 2.4 g (43.7%) of the diazonium salt in the usual way. M.p. 106° (decomp.).

Found %: Sn 19.50, 19.08. $(O_2NC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$. Calculated %: Sn 19.42.

Preparation of double diazonium salts of methyltin trichloride through the double diazonium salts of ferrous chloride. 1. To a solution of 3.5 g (0.018 mole) of p-$CH_3C_6H_4N_2Cl \cdot FeCl_3$ in the minimum amount of acetone was added in the cold a solution of 1.5 g (0.009 mole) of CH_3SnOOH in 17 ml of methanol saturated with hydrogen chloride. The precipitate of the double salt $(p\text{-}C_7H_7N_2Cl)_2 \cdot CH_3SnCl_3$ was filtered off and purified by reprecipitation with ether from methanol. Yield 1.7 g (34%), m.p. 112° (decomp.). An authentic sample of a double salt of this composition melts at 112° (decomp.).

2. From 6 g (0.018 mole) of p-$CH_3OC_6H_4N_2Cl \cdot FeCl_3$ and 1.5 g (0.009 mole) of CH_3SnOOH there was obtained, under conditions used in the foregoing experiment, 1.7 g (32.5%) of $(p\text{-}CH_3OC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$. M.p. 165° (decomp.). An authentic sample of the double salt of p-anisyldiazonium chloride and methyltin trichloride melts at 165° (decomp.).

3. From 6.8 g (0.018 mole) of p-$C_2H_5OCOC_6H_4N_2Cl \cdot FeCl_3$ and 1.5 g (0.009 mole) of CH_3SnOOH was obtained, under the usual conditions, 1.4 g (25%) of $(p\text{-}C_2H_5OCOC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$. M.p. 108° (decomp.). An authentic sample of this salt melts at 108° (decomp.).

Preparation of double salts of p-bromophenyldiazonium chloride and methyltin trichloride. 3.1 g (0.018 mole) of p-bromoaniline hydrochloride was dissolved in 15 ml of alcohol. To this solution was added 0.5 ml of alcoholic HCl followed by the gradual addition of 2.7 g (0.018 mole) of isoamyl nitrite with cooling in ice. The diazonium chloride solution was allowed to stand for 15 minutes after which a solution of 1.5 g of CH_3SnOOH (0.009 mole) in 17 ml of alcoholic HCl was added. The salt which precipitated was filtered off and purified by reprecipitation with ether from methanol. Yield 2.5 g (42%), m.p. 147° (decomp.). The authentic salt having the structure $(p\text{-}BrC_6H_4N_2Cl)_2 \cdot CH_3SnCl_3$ melts at 147° (decomp.).

Preparation of double diazonium salts of diethyltin dichloride. 1. To a solution of 1.1 g (0.008 mole) of aniline hydrochloride in 7.5 ml of alcohol was added 0.5 ml of alcoholic HCl and 0.94 g (0.008 mole) of isoamyl nitrite with cooling. To this diazo solution was added a solution of 1 g (0.004 mole) of $(C_2H_5)_2SnCl_2$ in 1 ml of alcohol. The precipitate of the double salt of phenyl diazonium chloride and diethyltin dichloride was filtered off and reprecipitated with ether from alcohol. Yield 2 g (94%), m.p. 80-81° (decomp.).

Found %: Sn 22.24, 22.22. $(C_6H_5N_2Cl)_2 \cdot (C_2H_5)_2SnCl_2$. Calculated %: Sn 22.45.

2. From 1.32 g (0.008 mole) of p-$ClC_6H_4NH_2 \cdot HCl$, dissolved in 5 ml of alcohol, and 1 g (0.004 mole) of $(C_2H_5)_2SnCl_2$ there was obtained 2 g (83% of the corresponding double diazonium salt. M.p. 98-99° (decomp.).

* Because of unsatisfactory results obtained with the usual method of analysis of organotin compounds for tin [5] when applied to double diazonium salts, the method has been modified somewhat. The decomposition of the salt was initiated in a quartz test tube by heating 0.5 g of the compound with 2-3 drops of water. To complete the decomposition a mixture of HNO_3 and H_2SO_4 (about 30 drops) was then added. The analysis was then continued in the usual way.

Found %: Sn 19.32, 19.63. $(ClC_6H_4N_2Cl)_2 \cdot (C_2H_5)_2SnCl_2$. Calculated %: Sn 19.86.

3. From 1.66 g (0.008 mole) of $p\text{-}BrC_6H_4NH_2 \cdot HCl$, dissolved in the minimum amount of alcohol, and 1 g (0.004 mole) of diethyltin dichloride there was obtained under the usual conditions, 1.85 g (68%) of the corresponding double salt. M. p. 110° (decomp.).

Found %: Sn 17.29, 16.89. $(BrC_6H_4N_2Cl)_2 \cdot (C_2H_5)_2SnCl_2$. Calculated %: Sn 17.29.

4. From 1.62 g (0.008 mole) of $p\text{-}C_2H_5OCOC_6H_4NH_2 \cdot HCl$, dissolved in 3.5 ml of alcohol and 1 g (0.004 mole) of $(C_2H_5)_2SnCl_2$ there was obtained, under the usual conditions, 2.3 g (85%) of the double salt. M.p. 80° (decomp.).

Found %: Sn 17.47, 17.30. $(p\text{-}C_2H_5OCOC_6H_4N_2Cl)_2 \cdot (C_2H_5)_2SnCl_2$. Calculated %: Sn 17.64.

5. From 1.2 g (0.008 mole) of $p\text{-}CH_3C_6H_4NH_2 \cdot HCl$, dissolved in the minimum amount of alcohol, and 1 g (0.004 mole) of $(C_2H_5)_2SnCl_2$ there was obtained, under the usual conditions, 1.6 g (74%) of the double salt. M.p. 88-89° (decomp.).

Found %: Sn 21.90. $(C_7H_7N_2Cl)_2 \cdot (C_2H_5)_2SnCl_2$. Calculated %: Sn 22.40.

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INVESTIGATION OF COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

XX. REACTION OF ETHYL ESTERS OF β-NITROPHENYLGLYCIDIC ACIDS AND p-CHLOROPHENYLGLYCIDIC ACID WITH AMMONIA AND ANILINE

V. F. Martynov and G. Ol'man

In one of our recent studies [1] we investigated the reaction of ethyl esters of β-phenylglycidic acids containing electron-donor substituents in the phenyl ring with ammonia and aromatic amines. In this work it was established that all phenylglycidic esters with electron-donor groups add amines in the same way as unsubstituted phenylglycidic esters, i.e., in the α-position. For a final resolution of the question of the effect of a substituent in the phenyl ring of glycidic acids on the place of opening of the oxide ring under the influence of amines it was necessary to investigate the β-phenylglycidic esters containing electron-accepting substituents in the phenyl ring. For this purpose we synthesized and investigated the ethyl esters of β-(p-nitrophenyl)-, β-(m-nitrophenyl)-, β-(o-nitrophenyl)-, and β-(p-chlorophenyl) glycidic acid.

All our attempts to add aniline and ammonia to the ethyl ester of β-(o-nitrophenyl) glycidic acid were unsuccessful. In the literature it is indicated [2] that this reaction is easily accomplished by the action of aniline with the sodium salt of β-(o-nitrophenyl) glycidic acid. We repeated the experiments of these authors and actually obtained the same product to which they ascribed the formula α-hydroxy-β-anilino-β-(o-nitrophenyl) propionic acid. However, the compound indicated split out aniline with extreme ease upon heating with barium hydroxide, which is characteristic only of aniline salts. In this connection we carried out a spectroscopic study in the infrared both of β-(o-nitrophenyl) glycidic acid itself and of its reaction product with aniline. In this study it appeared that the characteristic frequency for the oxide ring also was evident in the latter (Fig. 1). Consequently, in this case also addition of aniline to the oxide ring did not take place, and the product formed was the corresponding aniline salt.

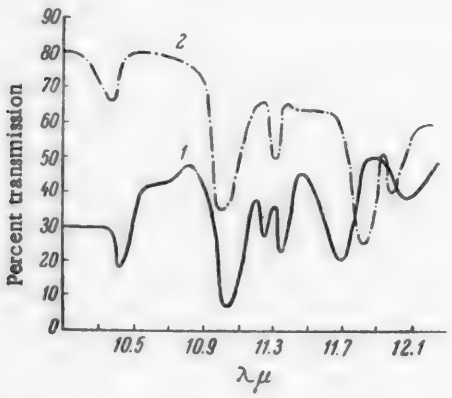
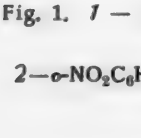


Fig. 1. *1* — o-$NO_2C_6H_4CH—CH—COOC_2H_5$;



2 — o-$NO_2C_6H_4CH—CH—COOH \cdot NH_2C_6H_5$.

The ethyl ester of β-(p-nitrophenyl) glycidic acid gave an addition product with aniline, although in small yield. With regard to the ethyl ester of β-(m-nitrophenyl) glycidic acid, the corresponding aniline addition product was obtained in 57% yield. The isolation of the reaction products in these two instances was very difficult. Purification by distillation was impossible because the boiling point was too high and explosive decomposition was possible. Precipitation (as the hydrochlorides) in anhydrous alcohol solution by passing gaseous hydrogen chloride through did not give positive results either, and only the use of concentrated hydrochloric acid, which was added to an alcohol solution of the reaction product previously freed of excess aniline, gave the desired result. On prolonged standing, the reaction products with aniline

separated out as hydrochlorides. For the ethyl ester of β-(p-chlorophenyl) glycidic acid the reaction with aniline proceeded rather easily and the addition product was obtained in good yield (60%).

The determination of the structure of the compounds mentioned was carried out by noting their behavior with concentrated sulfuric acid. If aniline added to the β-carbon atom, according to the general scheme found by us for the transformation of such compounds, then carbon monoxide should be evolved and the corresponding 2-phenylindole should form [3]. However, formation of the indoles was not observed for any of the aniline addition products obtained. On this basis it could be assumed with complete certainty that opening of the oxide ring in the glycidic acids investigated took place at the α-carbon atom and consequently we obtained the α--amino-β-hydroxy acids. The formulas of the compounds obtained are given in the table.

Ethyl ester of glycidic acid	Reaction product	
	with aniline	with ammonia
o-$NO_2C_6H_4$–CH(O)–CH–$COOC_2H_5$ (I)	—	o-$NO_2C_6H_4$–CH(O)–CH–CO–NH_2 (II)
m-$NO_2C_6H_4$CH(O)CH–$COOC_2H_5$ (V)	m-$NO_2C_6H_4$CH(OH)–CH(–HNC_6H_5)–$COOC_2H_5$ (VI)	m-$NO_2C_6H_4$–CH(NH_2)–CH(OH)–CO–NH_2 (VII)
p-$NO_2C_6H_4$–CH(O)–CH–$COOC_2H_5$ (III)	p-$NO_2C_6H_4$–CH(OH)–CH(NHC_6H_5)–$COOC_2H_5$ · HCl (IV)	p-$NO_2C_6H_4$–CH(O)–CH–$CONH_2$ (II)
p-ClC_6H_4–CH(O)–CH–$COOC_2H_5$ (VIII)	p-ClC_6H_4CH(OH)–CH(NHC_6H_5)–$COOC_2H_5$ (IX)	p-ClC_6H_4–CH(OH)–CH(NH_2)–$CONH_2$ (X)

Of the four glycidic esters investigated, only the ethyl esters of β-(m-nitrophenyl)- and β-(p-chlorophenyl) glycidic acids added ammonia. From the reaction of the β-(p-nitrophenyl)- and β-(o-nitrophenyl) glycidic esters with ammonia only the amides of these acids were obtained. It must be noted that this reaction, which was carried out with prolonged heating (to 100°) of a solution of the glycidic esters saturated with ammonia at 0°, proceeded with very severe tarring. The same phenomenon was observed in the investigation of the reaction of ammonia with phenylglycidic esters having electron-donor substituents in the phenyl ring [1]. In connection with the fact that the greater the electron-donor ability of the substituent in the phenyl ring, the smaller was the yield of the ammonia addition product in these cases, we assumed that apparently the amides of the β-hydroxy-α-aminopropionic acids obtained easily split out water in alkaline medium, and the amide of the unsaturated acid resinified.

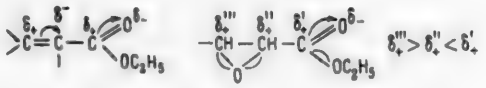
The delivery of electrons to the β-carbon atom naturally facilitates the splitting out of water and, on the contrary, its impoverishment of electrons as a result of the negative inductive effect of the chlorine in the β-(p-chlorophenyl) glycidic ester should decrease the tendency to splitting out of water from its ammonia addition product. If the formation of the unsaturated acid actually is the cause of resinification, then the reaction of ammonia with the β-(p-chlorophenyl) glycidic ester should proceed with less resinification and give a good yield of the addition product. This, however, was not observed. Attention is attracted by the fact that in all these instances the yield of addition product does not decrease in proportion to the heating of the reaction mixture, as should be expected if it were resinified, but on the contrary it increases. It is obvious that the glycidic esters themselves are unstable upon prolonged heating in alkaline solution. This also is confirmed by the marked resinification when they are saponified with alcoholic alkali.

Proof of the structure of the products of the addition of ammonia to the β-(m-nitrophenyl)- and β-(p-chlorophenyl) glycidic esters was carried out by the previously employed method of oxidation with lead

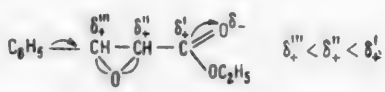
tetraacetate. As a result of the oxidation we obtained in the first case a material with a melting point close to that of m-nitrobenzonitrile. Comparison of its infrared spectrum with the spectrum of m-nitrobenzonitrile and m-nitrobenzaldehyde prepared by known methods showed definitely that the material was m-nitrobenzonitrile with some admixture of m-nitrobenzaldehyde.

In the case of the oxidation of the product of addition of ammonia to the β-(p-chlorophenyl) glycidic ester, p-chlorobenzaldehyde was obtained. In this same study it was shown that the β-(m-nitrophenyl) glycidic ester adds ammonia predominantly (87%) in the β-position, and the β-(p-chlorophenyl) glycidic ester adds it to the α-carbon atom.

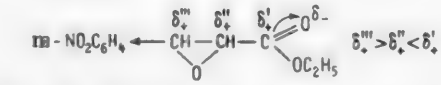
On the basis of our investigations on the opening of the oxide ring upon reaction of β-alkyl- and β-arylglycidic esters with ammonia and aniline, it is possible to attempt to explain the mechanisms discovered by us. At present this reaction is considered from the point of view of its mechanism as a nucleophilic S_N2 substitution [4]. As is known, the rate of such a reaction depends on the steric hindrances around the reaction center, the relative magnitude of its positive charge, and the nucleophilic nature of the molecule attacked. In our case we have two principal possibilities for the direction of attack, namely at the α- or the β-carbon atom. The main course of the reaction in one or the other direction depends on their relative speed, i.e. on the factors just enumerated. The addition of aniline to the β-carbon atom of the β-alkylglycidic esters naturally cannot be effected in the presence of a β-substituent. Therefore it remains to seek a reason in the relative magnitude of the positive charge of the α- and β-carbon atoms. It is known that the oxide ring is capable of transferring its linkage, although considerably less readily than the double bond. Moreover, it is indicated in the literature that the oxide ring can be coupled with a carbonyl group [5]. On this basis we can expect some similarity in the electron shifts in the β-alkylglycidic esters and the ethyl ester of crotonic acid, to which, as is known, nucleophilic agents add in the β-position. Taking into account that in the former the complete loss of any of the electrons of the octet without its disruption is impossible, these electron shifts can be represented by the following diagrams



In a similar manner it is possible to explain the addition of ammonia to all of the phenylglycidic esters studied by us. Owing to the fact that the oxide ring couples less readily than the double bond, the phenyl ring at the demand of the carbonyl group transfers to the β-carbon atom a greater electron density than is further transferred from it to the carbonyl



As a result of the fact that $\delta_+''' < \delta_+''$, ammonia is added to the relatively more positive α-carbon atom. It is clear that the presence in the para-position of a methyl or methoxy group should strengthen such an effect. In the case of the β-(m-nitrophenyl) glycidic ester the negative induction effect of the m-nitro group leads to impoverishment of the electrons of the β-carbon atom, and the ammonia is added principally in this position



The circumstance that the β-phenylglycidic ester adds ammonia to the α-carbon atom in spite of the total electron-accepting action of the chlorine, in our opinion supports the determining role of conjugation for the place of opening of the oxide ring. The positive effect of the chlorine linking causes a similar action, as also does the unsubstituted phenyl ring.

The addition of aniline in the α-position of all the β-arylglycidic esters studied by us apparently is explained by a specific mechanism connected with the presence of the phenyl ring in the attacked and attacking

molecules. The clarification of this mechanism is not yet possible. Obviously, however, the determining factor here is not an energy factor but a probability factor. The greater stability of the oxide ring in the β-(o-nitrophenyl) glycidic ester, most probably, is caused by the strong effect of the field of the o-nitro group, which makes possible the approach of the nucleophilic agent to the oxide ring.

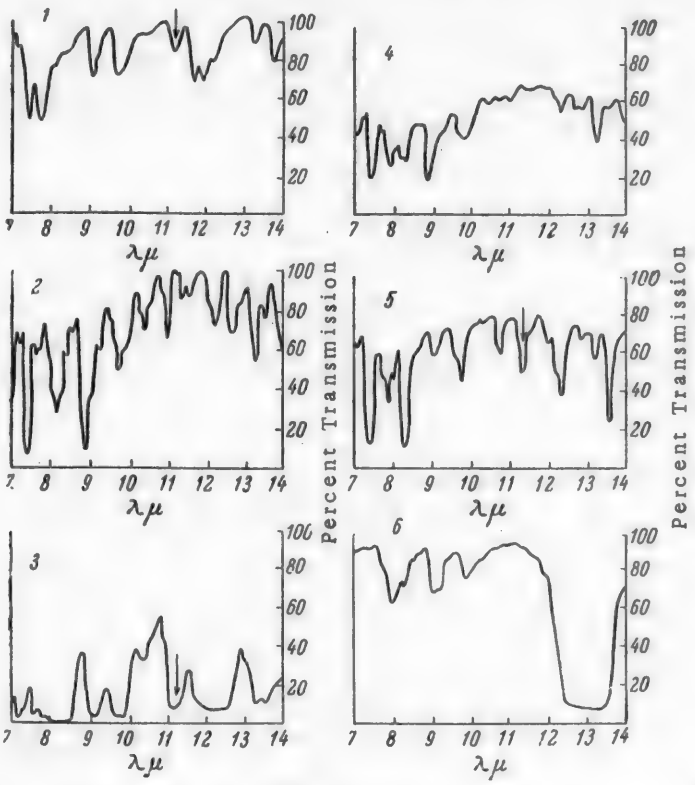


Fig. 2. *1* — p-$NO_2C_6H_4$—CH(O)—CHC(=O)—OC_2H_5, *2* — m-$NO_2C_6H_4$—CH(OH)—CH(NHC_6H_5·HCl)—C(=O)—OC_2H_5,

3 — p-ClC_6H_4—CH(O)—CH—C(=O)—OC_2H_5, *4* — p-$NO_2C_6H_4$—CH(OH)—CH(NHC_6H_5·HCl)—C(=O)—OC_2H_5,

5 — m-$NO_2C_6H_4$—CH(O)—CHC(=O)—OC_2H_5, *6* — p-ClC_6H_4—CH(OH)—CH(NHC_6H_5)—C(=O)—OC_2H_5.

We determined the infrared spectra for all the glycidic esters investigated by us and for their reaction products with aniline.* As can be seen from the spectra given (Fig. 2), all the glycidic esters have an absorption frequency in the region 887-906 cm^{-1} that disappears in the corresponding aniline addition products. Only in the case of the β-(o-nitrophenyl) glycidic ester was its disappearance not observed, which confirms our conclusion that reaction of this ester with aniline does not lead to opening of the oxide ring. We already had observed this same absorption frequency in the case of the β-arylglycidic esters with an electron-donor sub-

*The spectra were measured with an infrared spectrometer made in the Institute of Organo-Chemical Industry of the Ministry of Chemical Industry of the German Democratic Republic in Leipzig. Accuracy of the instrument was ±0.02μ. NaCl prism. Solid materials were measured in potassium bromide tablets.

stituent in the phenyl ring [1]. It seems to us, therefore, very probable that this particular frequency is characteristic of the oxide ring.

EXPERIMENTAL

Synthesis of the ethyl ester of β-(o-nitrophenyl) glycidic acid (I) was carried out by the method of Darzens. 75 g of β-o-nitrobenzaldehyde, 70 g of ethyl monochloroacetate, and 34 g of sodium ethylate were used. The reaction was carried out in absolute ether solution. After the usual treatment, the ether and the excess ethyl monochloroacetate were distilled off. The remaining liquid started to crystallize after a short period of standing. 60 g (56%) of a greenish material was obtained, which melted at 62.5° after two recrystallizations from alcohol. Upon distillation of the product (0.2 mm) it decomposed explosively around 170°.

Found %: N 6.1. $C_{11}H_{11}O_5N$. Calculated %: N 5.91.

Reaction of the Na salt of β-(o-nitrophenyl) glycidic acid with aniline. The reaction was carried out according to the instructions of Einhorn – Gernsheim. 1 g of β-(o-nitrophenyl) glycidic acid was dissolved in an aqueous solution of sodium carbonate. Then 0.5 g of aniline was added dropwise. After mixing, the solution became perfectly clear and was left for 24 hours. Upon acidification with hydrochloric acid a precipitate separated, which was filtered off and recrystallized from water. Pale yellow crystals were obtained with m.p. 125-127°. Upon heating with an aqueous solution of barium hydroxide the odor of aniline became evident. The crystals were charred by the action of concentrated sulfuric acid [like β-(o-nitrophenyl)-glycidic acid itself].

Found %: N 9.30. $C_{15}H_{14}O_5N_2$. Calculated %: N 9.28.

An attempt to add ammonia to the ethyl ester of β-(o-nitrophenyl) glycidic acid. A solution of 9 g of the ethyl ester in 30 ml of ethyl alcohol was saturated with ammonia at 0° and sealed in an ampoule. The ampoule was heated for 10 hours to 100°. The solution darkened greatly. The crystalline precipitate that formed, greatly contaminated with a tarry impurity, was recrystallized from dioxan and melted after this at 193-195°. 1.1 g of the amide of the glycidic acid (II) was obtained.

Found %: N 13.72. $C_9H_8O_4N_2$. Calculated %: N 13.46.

Synthesis of the ethyl ester of β-(p-nitrophenyl) glycidic acid (III) was carried out by the method of Darzens. 1 liter of absolute alcohol, 10 g of p-nitrobenzaldehyde, and 80 g of ethyl monochloroacetate were placed in a two-liter, three-necked flask. The reaction mixture was cooled to -12°, after which sodium ethylate (46 g) was added, with continuous stirring, in such a way that the temperature did not rise above -5°. After addition of the sodium ethylate was completed, the mixture was left at room temperature over-night, and then decomposed with water. The ether layer that separated was dried. After the ether was distilled off a dark red liquid remained that quickly crystallized. The crystals were pressed out and recrystallized from 80% ethyl alcohol. 55 g (35%) of barely yellowish crystals were obtained with m.p. 80°.

Found %: C 55.73; H 4.71; N 5.96. $C_{11}H_{11}O_5N$. Calculated %: C 55.69; H 4.64; N 5.90.

Preparation of the hydrochloride of the ethyl ester of β-anilino-α-hydroxy-β-(p-nitrophenyl) propionic acid (IV). 3 g of the ethyl ester of β-(p-nitrophenyl) glycidic acid and 4 g of freshly distilled aniline were dissolved in 40 ml of 96% ethyl alcohol and sealed in an ampoule that was heated for 10 hours at 140-150°. The contents of the ampoule had darkened considerably after this time. The ethyl alcohol and the unreacted aniline were steam-distilled off. The remaining brown mass was dissolved in alcohol and 10 ml of concentrated hydrochloric acid was added to the solution obtained. In several days a white precipitate separated from the mother liquor, the filtrate was drawn off, and the precipitate was washed with anhydrous alcohol. 0.5 g of barely greenish material was obtained with m.p. 173-174° (with decomp.).

Found %: N 7.85. $C_{17}H_{18}O_5N_2 \cdot HCl$. Calculated %: N 7.65.

Addition of ammonia to the ethyl ester of β-(p-nitrophenyl) glycidic acid. A solution of 5 g of the ethyl ester in 30 ml of ethyl alcohol, placed in an ampoule, was saturated with ammonia at 0°. The ampoule was then sealed and heated for 12 hours at 100°. The solution darkened greatly and a dark, crystalline precipitate formed that proved to be the amide of the glycidic acid. It was separated and recrystallized three times from dioxan. M.p. 209-210° (with decomp.).

Found %: N 13.24. $C_9H_8O_4N_2$. Calculated %: N 13.46.

Synthesis of the ethyl ester of β-(m-nitrophenyl) glycidic acid (V) was carried out by the method of Darzens. 100 g of m-nitrobenzaldehyde, 80 g of ethyl monochloroacetate, and 46 g of sodium ethylate were used. After the usual procedure for this method had been carried out, a thick, yellowish liquid was separated, which was then distilled in vacuo. B.p. 180-183° at 1 mm. After some standing it crystallized as white, needle-shaped crystals, which melted after recrystallization from ethyl alcohol at 55.5°. 5 g (35%) was obtained.

Found %: N 5.83. $C_{11}H_{11}O_5N$. Calculated %: N 5.906.

Preparation of the ethyl ester of β-hydroxy-α-anilino-β-(m-nitrophenyl) propionic acid (VI). 5 g of the ethyl ester of β-(m-nitrophenyl)-glycidic acid and 6 g of aniline were dissolved in 30 ml of anhydrous ethyl alcohol, after which the solution was placed in an ampoule that was heated for 18 hours at 130-150°. After completion of the reaction, the ethyl alcohol and the unreacted aniline were steam distilled off and the remaining tarry mass was dissolved in ethyl alcohol. 10 ml of concentrated hydrochloric acid was added to the alcohol solution. After some standing, a mass of white crystals precipitated, which were separated and washed with anhydrous ethyl alcohol and then with absolute ether. 4.5 g (57%) of the white crystals were obtained with m.p. 175-181° (with decomp.). When the crystals were mixed with sulfuric acid, hydrogen chloride was evolved. Upon heating with water the material became liquid.

Found %: N 7.75. $C_{17}H_{18}O_5N_2 \cdot HCl$. Calculated %: N 7.65.

The hydrochloric acid was removed by passing dry ammonia through a suspension in absolute ether of the salt prepared above. After completion of the passage of the ammonia, the ether solution was filtered off from the precipitate of ammonium chloride, the ether was distilled off, and the remaining tarry mass was immersed in a cooling mixture. After prolonged standing it crystallized completely. M.p. 86.0-86.5°.

Found %: N 8.65. $C_{17}H_{18}O_5N_2$. Calculated %: N 8.48.

Addition of ammonia to the ethyl ester of β-(m-nitrophenyl) glycidic acid. A solution of 5 g of the ethyl ester of the acid in 30 ml of anhydrous ethyl alcohol was saturated with ammonia at room temperature. After this the reaction mixture was sealed in an ampoule and heated for 15 hours at 100°. The solution darkened greatly, and upon cooling a crystalline precipitate separated that was considerably contaminated with a tarry impurity. The crystals were purified by repeated recrystallization from dioxan. 1 g of white, needle-shaped crystals was obtained with m.p. 180-181°.

Found %: N 13.49. $C_9H_8O_4N_2$. Calculated %: N 13.46.

A second sample of a solution of 3 g of the ethyl ester of β-(m-nitrophenyl) glycidic acid in 25 ml of ethyl alcohol, saturated at 0° with ammonia, was allowed to stand for 1 month at room temperature in an ampoule. The solution darkened considerably and on the walls of the ampoule pale yellow crystals were formed that were separated from the solution and washed with anhydrous alcohol. 0.5 g (17.5%) was obtained. M.p. 194°.

Found %: N 18.55. $C_9H_{11}O_4N_3$. Calculated %: N 18.66.

Oxidation with lead tetraacetate of the product of the addition of ammonia to the ethyl ester of β-(m-nitrophenyl) glycidic acid (VII). 0.4 g of the addition product described above and 2 g of freshly prepared lead tetraacetate were dissolved in 20 ml of glacial acetic acid. The solution was left for 2 days at room temperature. After this the acid was neutralized with sodium carbonate and the whole mixture was steam-distilled. The white, needle-shaped crystals that had distilled were separated. 0.20 g was obtained. M.p. 102-104°. The substance sublimed readily. Found %: N 17.08. It ensued from the infrared spectral investigation of the material that it was a mixture of m-nitrobenzonitrile (87%) and m-nitrobenzaldehyde (13%).

Synthesis of the ethyl ester of β-(p-chlorophenyl) glycidic acid (VIII). p-Chlorobenzaldehyde was prepared by the chlorination of p-chlorotoluene. The synthesis was carried out by Darzens' method. 100 g of p-chlorobenzaldehyde, 88 g of ethyl monochloroacetate, and 46 g of sodium ethylate were used for the reaction. The reaction was carried out in absolute ether solution (700 ml). After the usual treatment of the reaction mixture for this method 70 g (45%) of a liquid was obtained that was then distilled in vacuo.

B.p. 160° at 1 mm, d^{20}_4 1.2527, $n^{20}D$ 1.5458. MR_D 57.06; Calculated. 55.36; EMR_D 1.70.

Found %: C 58.30; H 4.73. $C_{11}H_{11}O_3Cl$. Calculated %: C 58.27; H 4.85.

Preparation of the ethyl ester of β-hydroxy-α-anilino-β-(p-chlorophenyl) propionic acid (IX). 5 g of the ethyl ester of β-(p-chlorophenyl) glycidic acid and 6 g of aniline were sealed in an ampoule, which was heated for 8 hours at 140-145°. The reaction mass was vacuum distilled. At 190° (1 mm) a pale yellow, thick liquid distilled, which crystallized upon long standing. 4 g (57%) was obtained.

Found %: N 4.25. $C_{17}H_{18}O_3NCl$. Calculated %: N 4.38.

Preparation of the amide of β-hydroxy-α-amino-β-(p-chlorophenyl) propionic acid (X). A solution of 10 g of the ethyl ester of β-(p-chlorophenyl) glycidic acid in 30 ml of ethyl alcohol was saturated with ammonia at 0° and sealed in an ampoule, which was held for 36 hours at room temperature and then heated at 100°. Upon cooling, a white crystalline precipitate separated out, which melted at 182° after recrystallization from aqueous alcohol. 1.7 g (18%) was obtained.

Found %: C 50.34; H 5.03; N 13.02. $C_9H_{11}O_2N_2Cl$. Calculated %: C 50.34; H 5.03; N 13.10.

Oxidation of the amide of β-hydroxy-α-amino-β-(p-chlorophenyl) propionic acid with lead tetraacetate. To a solution of 1.0 g of the amide in 25 ml of glacial acetic acid was added 3.5 g of freshly prepared lead tetraacetate. The reaction mixture was left at room temperature for two days. After this the acetic acid was neutralized with sodium hydroxide, whereupon a white crystalline precipitate separated out, which was pressed out and melted without additional purification at 40-42°. 0.46 g (70%) was obtained. From the crystalline precipitate a quantitative yield of phenylhydrazone was obtained with m.p. 125-126° (in the literature the m.p. 127° is given for the phenylhydrazone of p-chlorobenzaldehyde).

Found %: N 12.28. $C_{13}H_{11}N_2Cl$. Calculated %: N 12.15.

SUMMARY

1. The reactions of aniline and ammonia with the ethyl esters of β-(o-nitrophenyl)-, β-(m-nitrophenyl)-, β-(p-nitrophenyl)-, and β-(p-chlorophenyl) glycidic acids have been investigated.

2. It has been established that the ethyl esters of β-(m-nitrophenyl)-, β-(p-nitrophenyl)-, and β-(p-chlorophenyl) glycidic acids add aniline in the α-position. Ammonia is added to the β-(p-chlorophenyl) glycidic ester in the α-position, but to the β-(m-nitrophenyl) ester predominantly in the β-position. The β-(p-nitrophenyl) glycidic ester does not add ammonia at all.

3. It has been shown that the ethyl ester of β-(o-nitrophenyl) glycidic acid does not add either aniline or ammonia.

4. The reaction of the Na salt of β-(o-nitrophenyl) glycidic acid with aniline has been studied. It has been shown that in this case a product of addition to the oxide ring of the glycidic acid salt is not obtained. The data in the literature to the effect that the addition reaction takes place are erroneous.

5. The infrared spectra of all the aromatic glycidic esters investigated by us and of their aniline addition products have been determined. Absorption maxima have been marked that most probably are characteristic of the oxide ring.

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INVESTIGATION OF COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

XXI. REACTION OF AMIDES OF β-TETRA- AND β-PENTAMETHYLENEGLYCIDIC ACIDS WITH HEXYL- AND BENZYLAMINES

V. F. Martynov and Zh. D. Vasiutina

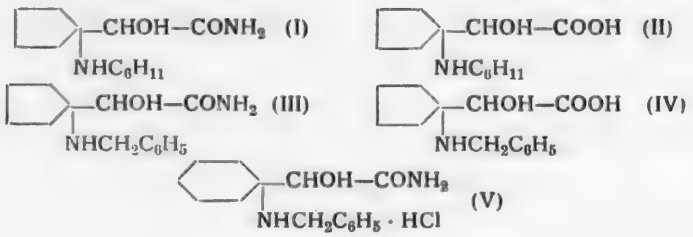
In one of the previous communications [1] an investigation of the reaction of aliphatic and aliphatic-aromatic amines with the amide of β,β'-dimethylglycidic acid has been described. The present work is a continuation of this investigation.

The reaction of the amides of β-tetra- and pentamethyleneglycidic acids and hexyl- and benzylamines was accomplished by heating their alcohol solutions in sealed ampoules at 100 or 120-130°. The more reactive proved to be the amide of β-tetramethyleneglycidic acid, which gave comparatively good yields of addition products with both amines. For purposes of comparison we carried out the reaction of cyclohexylamine with the potassium salt of β-tetramethyleneglycidic acid, but in this case a lower yield of the addition product was obtained. The amide of β-pentamethyleneglycidic acid appeared less reactive. With hexylamine, reaction did not take place at all, in spite of the fact that we carried out the reaction at 150°. It is obvious that such a result is explained by steric hindrances, by virtue of which the two cyclohexane rings, which as is known have a nonplanar structure, cannot rest in direct proximity to one another. This, by the way, again confirms that opening of the oxide ring of β-dialkyl-substituted glycidic acids occurs at the β-carbon atom, because otherwise the reaction might go in the direction of addition to the α-carbon atom, which however has never been observed. With benzylamine the reaction takes place, it is true, under somewhat more severe conditions (heating to 120-130°). In this case, as is understandable, the steric hindrances are considerably less active.

We attempted to prepare benzoyl derivatives for the addition products — the amides of the hydroxyamino acids that we obtained — but this attempt succeeded only with the addition product of cyclohexylamine to the potassium salt of β-tetramethyleneglycidic acid. By the Schotten-Baumann method [2] the corresponding N-benzoyl derivative was obtained.

For evidence of the structure of the addition products we took advantage of the action of concentrated sulfuric acid [1]. Upon heating the amide of hydroxycyclohexylamino-β-tetramethylenepropionic acid with sulfuric acid at 150-160°, copious evolution of gas bubbles (carbon monoxide) began, which to a certain extent already might indicate the structure of the addition compound. After the usual treatment of the reaction mixture, in these instances we succeeded in isolating α-cyclohexylamino-α-tetramethyleneacetaldehyde as its 2,4-dinitrophenylhydrazone. It was possible to conclude that the oxide ring in the indicated glycidic acid amide was opened at the β-carbon atom. Regrettably, this method of proof, which gives good yields of decomposition products for the addition products of aromatic amines, gives very low yields in the case of aliphatic amines. This is explained, in all probability, by the fact that the aminoaldehydes obtained in this way which contain aliphatic radicals undergo further conversion to resinous products, while the aminoaldehydes that contain aromatic radicals are stabilized as a result of conversion to indoles. We tried to decrease the temperature limits of the breakdown by using not the amides of the hydroxyamino acids, but the free acids; in this case breakdown set in at a lower temperature (100-120°); however, even under such experimental conditions an increase in yields of the aminoaldehydes was not observed.

The product obtained by reaction of the amide of β-tetramethyleneglycidic acid with benzylamine also was subjected, in the form of the free acid, to reaction with sulfuric acid. Decomposition with copious evolution of carbon monoxide took place at 100-110°. This indicated the presence of an α-hydroxy-β-amino acid; however, the nature of the second fragment of the molecule was not clarified by us. We ascribed a structure to the compound that was obtained by the reaction of the amide of β-pentamethyleneglycidic acid with benzylamine by analogy with the previously studied compounds. The structural formulas for the compounds obtained are presented below.



EXPERIMENTAL

Preparation of the amide of α-hydroxy-β-cyclohexylamino-β-tetramethylenepropionic acid (I). 5 g of the amide of β-tetramethyleneglycidic acid dissolved in 30 ml of anhydrous ethyl alcohol and 4.5 g of cyclohexylamine was sealed in an ampoule, which was heated for 6 hours at 100°. After the heating of the reaction mixture was completed, part of the ethyl alcohol (10-15 ml) was distilled off in vacuo. From the remaining liquid, crystals precipitated in several hours that melted at 127-128° after recrystallization from 96% alcohol. Yield 4.3 g (50.6%).

Found %: N 11.56. $C_{13}H_{24}O_2N_2$. Calculated %: N 11.67.

Decomposition of the amide (I) by the action of concentrated sulfuric acid. To 5 g of the compound was added 35 ml of concentrated sulfuric acid. The mixture was heated on a bare flame while being stirred. At 150-160° copious evolution of gas bubbles (carbon monoxide) began and the solution darkened. When the evolution of bubbles slowed down, the hot liquid was poured onto ice. When the reaction mixture was neutralized with sodium hydroxide solution, there separated out an emulsion of cyclohexylaminotetramethyleneacetaldehyde, which was steam-distilled off. The aminoaldehyde was extracted with ether from the distillate. After being dried with potash, the ether was distilled off and the residue was distilled in vacuo. At 140-144° (5 mm) a small amount of a viscous, yellowish liquid passed over, which was combined with 2,4-dinitrophenylhydrazine. As a result, crystals of the 2,4-dinitrophenylhydrazone of cyclohexylaminotetramethyleneacetaldehyde precipitated, which melted at 123-125° after recrystallization from ethyl alcohol.

Found %: N 18.96. $C_{18}H_{25}O_4N_5$. Calculated %: N 18.67.

Preparation of α-hydroxy-β-cyclohexylamino-β-tetramethylenepropionic acid (II). 3 g of the amide of α-hydroxy-β-cyclohexylamino-β-tetramethylpropionic acid was refluxed with 50 ml of 50% sulfuric acid for 8 hours. The sulfuric acid was precipitated with barium carbonate until there was a negative reaction for $SO_4^{=}$ ion. The filtrate was evaporated on a water bath. As a result, white crystals of the hydroxyamino acid were obtained, which melted at 206-207° (with decomp.) after recrystallization from water. 1.75 g (58%) was obtained.

Found %: N 5.95. $C_{13}H_{23}O_3N$. Calculated %: N 5.81.

Preparation of the potassium salt of β-tetramethyleneglycidic acid. To a solution of 3.5 g of potassium hydroxide in anhydrous ethyl alcohol was added 10 g of the ethyl ester of β-tetramethyleneglycidic acid. Almost at once a white precipitate of the potassium salt of β-tetramethyleneglycidic acid separated. The yield was quantitative.

Reaction of the potassium salt of β-tetramethyleneglycidic acid with cyclohexylamine. 5 g of the potassium salt of β-tetramethyleneglycidic acid and 3.5 g of cyclohexylamine were dissolved in anhydrous ethyl alcohol. The solution obtained was sealed in an ampoule that was heated at 100° for 6 hours. As a result

of the reaction, a dark, viscous liquid was obtained that started to crystallize in a few days. 2.6 g (34%) of the potassium salt of α-hydroxy-β-cyclohexylamino-β-tetramethylenepropionic acid was obtained.

Preparation of the benzoyl derivative of α-hydroxy-β-cyclohexylamino-β-tetramethylenepropionic acid was carried out by the Schotten-Baumann method [2]. 0.5 g of the potassium salt of α-hydroxy-β-cyclohexylamino-β-tetramethylenepropionic acid was dissolved in a small amount of 10% aqueous NaOH solution. To this solution was added gradually an excess (0.4 g) of benzoyl chloride. The mixture was shaken vigorously. The unreacted benzoyl chloride was decomposed by heating on the water bath. The precipitate of benzoyl derivative that had been formed was filtered off, washed with water until the alkali was completely removed, and dissolved in aqueous ethyl alcohol. To the solution obtained there was added dilute hydrochloric acid (1 : 1), after which a white precipitate separated out, which was filtered off and recrystallized from 40-45% aqueous ethyl alcohol. 0.21 g of the benzoyl derivative was obtained, which amounted to 34%.

Found %: N 4.5. $C_{20}H_{27}O_4N$. Calculated %: N 4.06.

Preparation of the amide of α-hydroxy-β-benzylamino-β-tetramethylenepropionic acid (III). 5 g of the amide of β-tetramethyleneglycidic acid and 4.7 g of benzylamine were dissolved in 20 ml of anhydrous ethyl alcohol and sealed in an ampoule that was heated for 8 hours at 100°. The next day crystals of the amide precipitated. Yield 4.2 g (48%). After recrystallization from 96% ethyl alcohol the compound melted at 53-54°.

Found %: N 11.45. $C_{14}H_{20}O_2N_2$. Calculated %: N 11.29.

Preparation of α-hydroxy-β-benzylamino-β-tetramethylenepropionic acid (IV). 2 g of the amide (III) was refluxed with 50 ml of 50% sulfuric acid for 8 hours. The sulfuric acid was neutralized by boiling the solution with barium carbonate until there was a negative reaction for $SO_4^{=}$ ion. The filtrate was evaporated on a water bath. 1.1 g (55%) of the acid was obtained. After recrystallization from ethyl alcohol the melting point in a sealed capillary was 228-229° (with decomp.).

Found %: N 5.75. $C_{14}H_{19}O_3N$. Calculated %: N 5.62.

Preparation of the amide of α-hydroxy-β-benzylamino-β-pentamethylenepropionic acid (V). A mixture of 5 g of the amide of pentamethylenepropionic acid dissolved in 30 ml of ethyl alcohol with 4 g of benzylamine was sealed in an ampoule and heated for 8 hours at 120-130°. A dark, viscous liquid was obtained that did not crystallize upon prolonged standing. From this reaction mass the unreacted benzylamine was steam distilled off, after which concentrated hydrochloric acid was added to the residue. A white precipitate of the hydrochloride of the amide separated out. 3.2 g (33%) was obtained. After recrystallization from aqueous alcohol the m.p. was 222-223° (with decomp.).

Found %: N 9.43. $C_{15}H_{23}O_2N_2Cl$. Calculated %: N 9.38.

SUMMARY

1. The reaction of the amides of β-tetra- and β-pentamethyleneglycidic acids with cyclohexyl- and benzylamines has been studied. It has been found that the amide of β-tetramethyleneglycidic acid is more reactive than the amide of β-pentamethyleneglycidic acid.

2. It has been shown that opening of the oxide ring of the amides of the indicated glycidic acids occurs at the α-carbon atom. All the addition products were prepared for the first time.

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REACTIONS OF HALOMETAL ALCOHOLATES

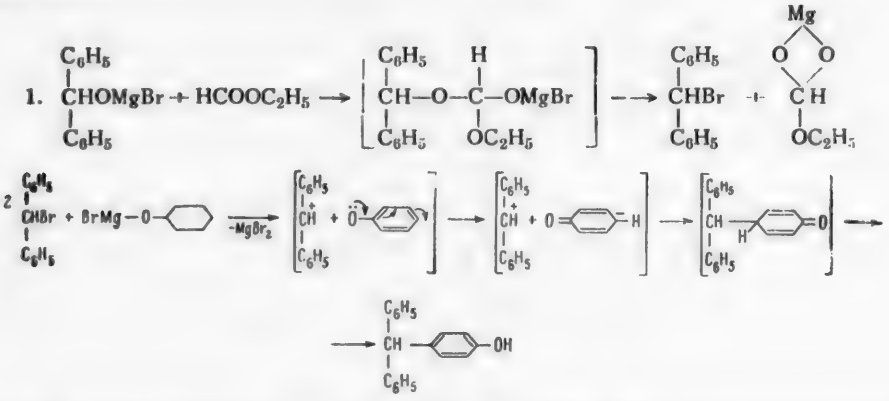
VI. A NEW METHOD OF SYNTHESIS OF MONOHYDROXYTRIARYLMETHANES

I. I. Lapkin and M. I. Belonovich

As a result of previous investigations [1] it has been established that the action on halomagnesium diarylcarbinolates of esters of formic or oxalic acid used in equimolecular amounts with respect to the carbinolate leads to the formation of diarylmethyl halides. It also has been established that halomagnesium phenolates and naphtholates under the same conditions do not react with the esters mentioned. This circumstance was used by us to work out a method for the preparation of monohydroxytriarylmethanes.

The essence of this method is that a mixture of the diarylcarbinol and phenol or naphthol is converted by the addition of the appropriate amount of ethylmagnesium bromide to a mixture of bromomagnesium diarylcarbinolate and phenolate. Subsequent addition to the reaction mixture of an ester of oxalic acid converts the bromomagnesium diarylcarbinolate to diarylmethyl bromide, which, reacting with the bromomagnesium phenolate (or naphtholate) that is unchanged under these conditions, forms a monohydroxytriarylmethane.

As an intermediate product in this reaction we might suggest the formation of an aryl diarylmethyl ether, which rearranges then to the hydroxytriarylmethane, but since this ether has not been detected in the reaction products, the mechanism of the reaction under investigation may be represented by the following more probable scheme



That the ethers are not intermediate products of this reaction is also indicated by the fact that the products of carbinol or phenol rearrangements discovered by Schorigin [2] and characteristic of the specific group of ethers were not observed in the reaction studied.

A great deal of work has been devoted to the investigation of the condensation of aromatic alcohols with phenols. Some facts also have been recorded concerning the condensation of benzhydrol (and benzhydryl halides) with phenols. It has been established [3] that upon heating phenol and diphenylmethyl bromide on a water bath p-hydroxytriphenylmethane is formed, while heating sodium phenolate with this bromide leads to the formation of o-hydroxytriphenylmethane. The experiments of Schorigin [4] have shown that by the action of diphenylmethyl bromide on sodium phenolate there is produced, in addition to the phenyl ether of benzhydrol,

a small amount of o-hydroxytriphenylmethane. The reaction of benzhydrol and phenol in benzene solution and in the presence of $SnCl_4$ [5] leads to the formation of p-hydroxytriphenylmethane. Experiments [6] investigating the reaction of diphenylmethyl chloride with phenol in the presence of $ZnCl_2$ at 110° also led to these results. p-Hydroxytriphenylmethane also is obtained from benzhydrol and phenol in carbon bisulfide in the presence of $AlCl_3$ [7]. A similar condensation takes place with p-cresol. Upon heating benzhydryl bromide with p-cresol at 150° or with sodium p-cresolate at 50-60°, and also upon boiling with sodium p-cresolate in ether, 3-methyl-6-hydroxytriphenylmethane is obtained [3]. The reaction of benzhydrol with o-cresol in a mixture of glacial acetic acid and sulfuric acid on a boiling water bath results in the formation of 3-methyl-2-hydroxytriphenylmethane [8].

In contrast to the results of investigations [3] and [4], according to which o-hydroxytriphenylmethane is formed by the reaction of diphenylmethyl bromide with sodium phenolate, in the reaction under investigation of bromomagnesium phenolate and also of bromomagnesium o-cresolate with diphenylmethyl bromide, which is obtained as indicated above in the reaction of bromomagnesium benzhydrolate and the esters of oxalic acid, the p-isomers of hydroxytriarylmethanes are produced, and to be precise, p-hydroxytriphenylmethane. The ortho-isomers are produced only if the para-position is occupied. For example, when p-cresol is used in the reaction under study, 5-methyl-2-hydroxytriphenylmethane is formed, i.e. the benzhydryl radical is in the ortho-position relative to the hydroxyl group. This same radical when it enters into the α-naphthol molecule, occupies the 4-position, and in the β-naphthol molecule the α-position.

EXPERIMENTAL

1. Synthesis of 4-hydroxytriphenylmethane. Benzhydrol and phenol (1/15 mole each) were dissolved in three times their volume of anhydrous diethyl ether and to this solution was added an ether solution (3 volumes) of ethylmagnesium bromide (2/15 mole). To the resulting ether solution of bromomagnesium benzhydrolate and phenolate was added diethyl oxalate (1/15 mole), after which the reaction mixture was heated for 3 hours, then decomposed with water and 10% acetic acid, the ether layer was separated from the water and washed with a 10% sodium bicarbonate solution and water. After the ether solution was dried with calcined sodium sulfate, the solvent was distilled off and the reaction product was distilled in vacuo. The main fraction (13 g), which distilled at 190-200° (7 mm), crystallized in the receiver and was purified by recrystallization from petroleum ether. M.p. 110°. Yield 76%.

Found %: C 87.57; H 6.16; OH 6.1. $C_{19}H_{16}O$. Calculated %: C 87.66; H 6.20; OH 6.5.

In the literature m.p. 109° [5] and 112° [3] are indicated for 4-hydroxytriphenylmethane.

2. 3-Methyl-4-hydroxytriphenylmethane was prepared under the conditions indicated above and with the same amounts of the starting materials; instead of phenol, o-cresol was used. The reaction product was distilled in vacuo (6 mm) at 195-205°. By recrystallization from a mixture of petroleum ether and toluene (3 : 1) colorless crystals were obtained with m.p. 102°. Yield 12 g (66%). In the literature the m.p. 100° is indicated [9] for 3-methyl-4-hydroxytriphenylmethane prepared from 3-methyl-4-hydroxytriphenylcarbinol by boiling with zinc and glacial acetic acid.

Found %: C 87.38; H 6.49; OH 6.00. $C_{20}H_{18}O$. Calculated %: C 87.55; H 6.62; OH 6.20.

3. Synthesis of 5-methyl-2-hydroxytriphenylmethane. The reaction conditions were as indicated above. The starting materials — benzhydrol and p-cresol — were used in amounts of 1/15 mole. After vacuum distillation the reaction product was purified by recrystallization from a mixture of petroleum ether and toluene (3 : 1) and showed a m.p. of 135°. Yield 12.5 g (70%). According to [3], m.p. 135°.

Found %: C 87.35; H 6.45; OH 6.1. $C_{20}H_{18}O$. Calculated %: C 87.55; H 6.62; OH 6.2.

4. Synthesis of diphenyl-(4-hydroxynaphthyl-1)methane. The starting materials — benzhydrol, α-naphthol, and diethyl oxalate — were used in amounts of 2/15 mole. Since diphenyl-(4-hydroxynaphthyl-1) methane decomposes on vacuum distillation, the crystalline reaction product was purified by recrystallization from a mixture of petroleum ether and toluene. M.p. 171-172°. Yield 70%. According to [10], m.p. 170--171.5°.

Found %: C 88.78; H 5.76; OH 5.40. $C_{23}H_{18}O$. Calculated %: C 89.00; H 5.85; OH 5.50.

5. Synthesis of diphenyl-(2-hydroxynaphthyl-1)methane was carried out under the conditions indicated in the preceding experiments, from bromomagnesium benzhydrolate, β-naphtholate, and diethyl oxalate (1/15 mole each). After the ether was distilled off, the compound crystallized and was purified by recrystallization. M.p. 110° (from a mixture of petroleum ether and toluene). Yield 18 g (70%).

Found %: C 88.81; H 5.71; OH 5.20. $C_{23}H_{18}O$. Calculated %: C 89.00; H 5.85; OH 5.50.

For proof of the structure of the compound obtained, diphenyl-(2-ethoxynaphthyl-1) carbinol was first synthesized from benzophenone and 2-ethoxynaphthylmagnesium bromide (1/15 mole each) under the usual conditions for organomagnesium reactions. M.p. 156° (from a mixture of petroleum ether and toluene). Yield 40 g (56%).

Found %: C 84.52; H 6.18; OH 4.70; OC_2H_5 11.8. $C_{25}H_{22}O_2$. Calculated %: C 84.71; H 6.26; OH 4.80; OC_2H_5 12.7.

By heating the diphenyl-(2-ethoxynaphthyl-1) carbinol, dissolved in 98% acetic acid, with zinc dust for 3 hours diphenyl-(2-hydroxynaphthyl-1)-methane was obtained. M.p. 110°.

Found %: C 88.79; H 5.72; OH 5.3. $C_{23}H_{18}O$. Calculated %: C 89.00; H 5.85; OH 5.5.

A mixed melting point test with the compound obtained by the reaction under investigation showed no depression.

SUMMARY

1. A new method has been developed for the synthesis of monohydroxytriarylmethanes which is based on the action of oxalic acid esters on an equimolecular mixture of bromomagnesium diarylcarbinolates and phenolates (or naphtholates), and mechanisms have been shown for this reaction.

2. In this investigation two compounds not previously described were synthesized – diphenyl-(2-hydroxynaphthyl-1) methane and diphenyl-(2-ethoxynaphthyl-1) carbinol.

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METALLOORGANIC SYNTHESIS OF DIBIPHENYLALKANES AND DIPHENYLALKANES. III

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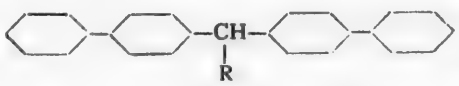
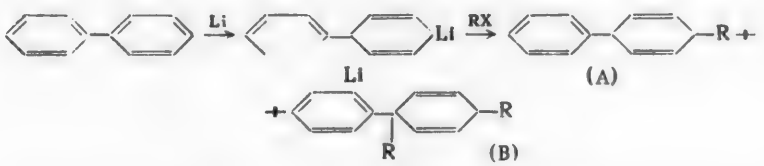
In preceding communications [1,2] the synthesis of hydrocarbons of the dibiphenylalkane and alkyl-1,4-dihydrodiphenyl series has been described. In the present communication the results are reported of additional investigations on the synthesis of these series of hydrocarbons. By the reaction of 4-diphenylmagnesium bromide with the ethyl ester of undecylenic and palmitic acids, alcohols were obtained which were dehydrated to olefins and then hydrogenated stepwise over Raney nickel to naphthenic hydrocarbons. The freezing points and the viscosities at different temperatures were determined for the hydrocarbons obtained. It was established that with lengthening of the alkyl radical up to a certain limit, in spite of the increase of molecular weight, the freezing point falls, but then rises sharply



	freezing point
CH_3	+46°
C_3H_7	+20
C_7H_{15}	+2
$C_{10}H_{21}$	−3
$C_{15}H_{31}$	+55

The viscosity of the hydrocarbons decreases with an increase in the alkyl chain, but the index of viscosity is almost unchanged (Fig. 1). According to the work of Schlenk and Bergmann [3] lithium is added to diphenyl in the 1,4-position, forming 1,4-dilithiumdihydrodiphenyl. By the action on the latter of n-C_4H_9Br and n-$C_{10}H_{19}Br$, we obtained monoalkyldihydrodiphenyls and dialkyldihydrodiphenyls.



All the 4-monoalkyl-1,4-dihydrodiphenyls solidify in crystalline form, but 1,4-dialkyl-1,4-dihydrodiphenyls, in spite of the large molecular weight, have freezing points considerably lower and solidify in the form of a glass.

R	m.p. (A)	F.p. (B)
C_4H_9	−1°	−19° (glass)
C_6H_{13}	+7	−25 (glass)
$C_{10}H_{21}$	+36	−17 (glass)

To establish the position (1 or 4) of the alkyl chain in the monoalkyldihydrodiphenyls, the dehydrogenation of n-C_4H_9- and n-C_6H_{13}-1,4-dihydrodiphenyls was carried out with sulfur. The 4-butyl- and 4-hexyldiphenyls agreed well as to freezing point with the freezing points of these hydrocarbons prepared previously by another method [4]. This indicates that the alkyl chains in the monoalkyldihydrodiphenyls are in the 4-position.

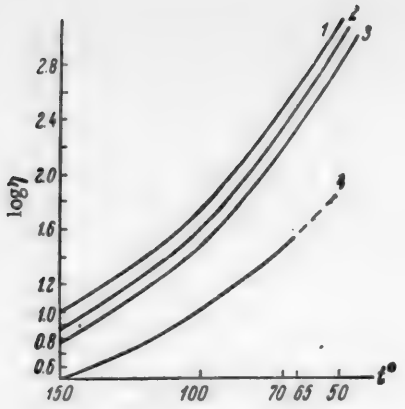
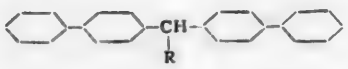


Fig. 1. Viscosity curves of hydrocarbons:



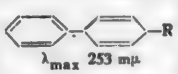
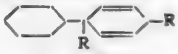
1 — R = C_3H_7, 2 — R = C_7H_{15}, 3 — R = $C_{10}H_{21}$, 4 — R = $C_{18}H_{37}$.

Ultraviolet absorption spectra* were determined for the compounds synthesized. The spectra of the mono- and disubstituted compounds were similar to each other and differed only in the intensity of the principal band (see Table). The spectra obtained raise doubts as to the correctness of the structure ascribed to the compounds synthesized. If we compare the spectra of our compounds (Fig. 2) with the spectra of diphenyl and 1-phenylcyclohexene, their similarity can be definitely seen, particularly in the magnitude of the intensity at the maximum.

From the literature it is known that the intensity of the band ~250 – 260 mμ in aromatic compounds does not exceed 300 units for a single ring, but it increases considerably when this ring is conjugated with the C = C, C = O, and other bonds. For example, the intensity of the maximum of the band in toluene is ~250, in triphenylmethane 900, and in styrene 12,000 units. In diphenyl, where there are conjugated C = C bonds, the intensity of the band is 20,000. In our compounds, to which we had up to now, following Schlenk and Bergmann [3], ascribed an unconjugated structure (quinoid structure of the II ring), the intensity also proved to be 20,000.

Recently Benkeser and co-workers [5], investigating the reduction of aromatic compounds with lithium in the medium of aliphatic amines, suggested the possible isomerization of the 1,4-dihydroaromatic compounds obtained to the more stable conjugated systems. Thus, when lithium acted on diphenyl, 1-cyclohexylcyclohexene was formed. When anisole was reduced [6], a mixture was obtained consisting of 53% 2,5-dihydroanisole and 47% 2,3-dihydroanisole.

Intensity of Maximum of Principal Absorption Band

Meaning of R	 λ_{max} 253 mμ	 λ_{max} 248 mμ
C_4H_9	24000	16200
C_6H_{13}	17000	10000
tert.-C_8H_{17}	21000	14000
iso-.C_8H_{17}	24000	13000
C_9H_{19}	17000	12000
$C_{10}H_{21}$	20000	6000

Examining the data obtained by us from the UV spectra, we can propose that in our case also partial isomerization took place with the formation of a mixture of 4-alkyl-1,4-dihydrodiphenyl and 4-alkyl-2,3-dihydrodiphenyl. With such an assumption, obviously, we should expect spectra similar to the diphenyls both in position and in intensity. For the disubstituted compounds there also is possible the formation of a mixture of 1,4-dialkyl-1,4-dihydrodiphenyl with other isomers of the dialkyldihydrodiphenyls (for example, with 3,4-dialkyl-3,4-dihydrodiphenyl), which probably explains also the sharp lowering of the freezing point of the dialkyldihydrodiphenyls. The intensity of the principal band also is changed depending on the percentage composition of the isomers.

*UV spectra were determined by I. N. Lifanova, for which the authors express their deep appreciation. The spectra were taken in an ISP-22 spectrograph in isooctane solution. A hydrogen lamp of the Ostroumov type was used as a uniform source of emission.

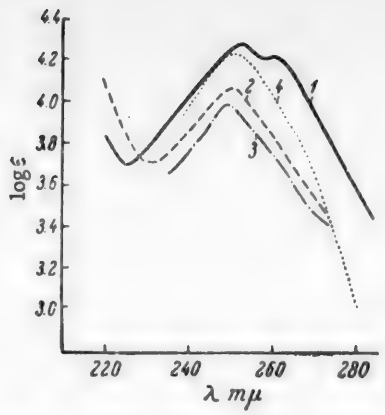
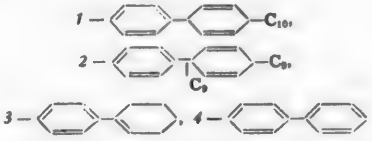


Fig. 2. Ultraviolet absorption spectra.



EXPERIMENTAL

1. Synthesis of dibicyclohexyldecylmethane. a) Preparation of dibiphenylundecadiene. To 20 g of Mg in 100 ml of ether was added over a period of 12 hours at 30-33° 257 g of 4-bromodiphenyl dissolved in 700 ml of ether. Then 106 g of ethyl undecylenate was added, after which the reaction mixture was stirred for 12 hours more at 40-45°. It was decomposed with 10% CH_3COOH. The ethereal portion of the solution was separated and the insoluble tetraphenyl was filtered off. 50 g of a product with b.p. 300-330° at 3 mm was isolated which represented, according to its analysis, a mixture of olefin and alcohol. To obtain the pure olefin the mixture was dehydrated with CH_3COOH and H_2SO_4 [7]. The olefin, distilled over sodium, had a b.p. of 295-298° at 3 mm.

Found %: C 92.18, 92.20; H 7.16, 7.14. $C_{35}H_{36}$. Calculated %: C 92.10; H 7.89.

b) Hydrogenation of the double bond in the chain. In an autoclave with a volume of 0.5 l were placed 15 g of olefin, 100 ml of dimethylcyclohexane, and 3 g of Raney nickel. The initial pressure was 60 atm., hydrogenation temperature 200°. A vaseline-like product was obtained with b.p. 300° at 3 mm.

Found %: C 91.72, 91.85; H 8.31, 8.22. $C_{35}H_{40}$. Calculated %: C 91.30; H 8.69.

c) Hydrogenation of aromatic rings. In an autoclave were placed 13 g of hydrocarbon, 140 ml of dimethylcyclohexane, and 6 g of Raney nickel. Initial pressure 100 atm, hydrogenation temperature 230-250°. The dibicyclohexyldecylmethane had a b.p. of 270-272° at 3 mm.

F.p. −3°, $n^{20}D$ 1.5080, ν_{50} 5.7595 st.•, ν_{100} 0.2840 st., ν_{150} 0.0610 st.

Found %: C 87.02, 87.12; H 13.01, 13.01. $C_{35}H_{64}$. Calculated %: C 86.77; H 13.22.

2. Synthesis of dibicyclohexylpentadecylmethane. a) Preparation of dibiphenylpentadecenemethane was carried out under the same conditions as in the preceding synthesis. From 24 g of Mg and 344 g of 4-bromodiphenyl dissolved in 700 ml of ether and 142 g of ethyl palmitate was obtained 40 g of a crystalline product representing a mixture of olefin and alcohol. The pure olefin was obtained by dehydration with acetic and sulfuric acids.

b) Dibiphenylpentadecylmethane was obtained by hydrogenation of the corresponding olefin. 13 g of hydrocarbon, 100 ml of dimethylcyclohexane, and 3 g of Raney Ni were used in the charge. Initial pressure 100 atm, hydrogenation temperature 200°. A hydrocarbon was obtained with m.p. 120°.

Found %: C 90.12, 90.23; H 10.00, 9.87. $C_{40}H_{50}$. Calculated %: C 90.56; H 9.43.

c) Hydrogenation of aromatic rings. 10 g of hydrocarbon, 100 ml of dimethylcyclohexane, and 6 g of Raney Ni were used in the charge. Initial pressure 110 atm, hydrogenation temperature 235-250°. The dibicyclohexylpentadecylmethane obtained had a m.p. of 55°.

ν_{100} 0.1018 st., ν_{150} 0.0340 st.

Found %: C 86.77, 86.80; H 13.10, 13.11. $C_{40}H_{74}$. Calculated %: C 86.66; H 13.33.

3. Reaction of 1,4-dilithium-1,4-dihydrodiphenyl with n-butyl bromide. A description of the experiment has been given in a preceding communication [2]. In the reaction 77 g of diphenyl, 7 g of lithium, and 400 ml of ether were used. The mixture was shaken for 80 hours. 137 g of n-butyl bromide was added. A total of 35 g of alkylbiphenyls was obtained. After repeated distillation 20 g of 4-butyl-1,4-dihydrodiphenyl was isolated, b.p. 152° at 3 mm.

•st. = stoke — publisher's note.

Found %: C 90.59, 90.44; H 9.52, 9.33. $C_{16}H_{26}$. Calculated %: C 90.56; H 9.43.

15 g of 1,4-dibutyl-1,4-dihydrodiphenyl also was isolated with b.p. 189° at 3 mm.

$n^{20}D$ 1.5272, d^{20}_4 0.9285, MR_D 88.76; calculated 88.91.

Found %: C 89.18, 89.11; H 10.82, 10.90. $C_{20}H_{32}$. Calculated %: C 89.55; H 10.45.

Dehydrogenation of 4-butyl-1,4-dihydrodiphenyl. 5 g of hydrocarbon and 0.6 g of sulfur were heated for 4 hours at 200-220°. The hydrocarbon was distilled over sodium. The 4-butyldiphenyl had a b.p. of 140° at 3 mm, f.p. +15°. Literature data [4]: f.p. +16°, $n^{20}D$ 1.5739.

4. Reaction of 1,4-dilithium-1,4-dihydrodiphenyl with n-decyl bromide. For the reaction 7.5 g of lithium, 77 g of diphenyl, and 600 ml of ether were taken. Shaking was continued for 80 hours. 105 g of n-decyl bromide was added. 29 g of alkylbiphenyls were obtained. Isolated: 4-n-decyl-1,4-dihydrodiphenyl, 19 g, b.p. 220-222° at 3 mm.

Found %: C 89.71, 89.51; H 10.55, 10.49. $C_{22}H_{32}$. Calculated %: C 89.18; H 10.81.

1,4-Di-n-decyl-1,4-dihydrodiphenyl, 10 g.

$n^{20}D$ 1.5040; d^{20}_4 0.8964, MR_D 143.68; calculated 143.0.

Found %: C 87.59, 87.62; H 12.44, 12.40. $C_{32}H_{52}$. Calculated %: C 88.07; H 11.93.

5. Dehydrogenation of 4-hexyl-1,4-dihydrodiphenyl was carried out under the same conditions as for 4-butyl-1,4-dihydrodiphenyl. The 4-hexyldiphenyl had a m.p. of 25°. Literature data [4]: m.p. +28°.

SUMMARY

1. Dibicyclohexyldecylmethane and dibicyclohexylpentadecylmethane have been synthesized. Their viscosity characteristics have been determined.

2. 4-Butyl-, 1,4-dibutyl-, 4-decyl-, and 1,4-didecyl-1,4-dihydrodiphenyl have been prepared.

3. The UV spectra of 12 alkyl-1,4-dihydrodiphenyls have been determined and it has been shown that in the organolithium synthesis of the indicated forms conjugated structures are produced for the most part, along with compounds having a quinoid structure.

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SILICOALKYLATION OF AROMATIC COMPOUNDS BY DICHLOROALKYL-SILANE CHLORIDES

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The possibility of silicoalkylation of various aromatic compounds by chloroalkyltrichlorosilanes and chloroalkyl(alkyl)dichlorosilanes in the presence of $AlCl_3$ or metallic aluminum was demonstrated earlier by us [1,2]. In these investigations it was shown that silicoalkylation products are formed with yields of 30-80%, and a qualitative evaluation of the reactivity of chloroalkyl(alkyl)silane chlorides of various structures was given.

Continuing these investigations, we studied the silicoalkylation of benzene, toluene, and chlorobenzene by dichloroalkylsilane chlorides. The course of these reactions was more complex. Yields of silicoalkylation products in this case proved to be lower (they varied from 3 to 48%), partly owing to a greater degree of resin formation. Furthermore, not only the yields, but also the character of the silicoalkylation products varied in dependence on the nature of both components, as is evident from Table 1, given in the experimental part.

It is of interest to note that in the case of α,α-, β,β-, and α,β-dichloroethyltrichlorosilanes chlorobenzene reacts mainly with both chlorine atoms of the dichloroalkyltrichlorosilane, and with yields about 3 times higher than for benzene. Toluene also reacts with a high yield, but mainly with one chlorine atom; the other chlorine atom is displaced by hydrogen in this case. It is known that toluene is a rather active hydrogen donor. Considerable resin formation is noted in all reactions with toluene. Displacement of chlorine by hydrogen did not occur with dichloromethylsilane chlorides.

In a reaction with α,β-dichloroethyltrichlorosilane (I), in which an aryl radical displaced one chlorine atom, and the second was reduced by hydrogen, $\geq Si-\underset{\underset{CH_3}{|}}{CH}-C_6H_4R$ (A), $\geq SiCH_2CH_2C_6H_4R$ (B), or a mixture of these could be formed. The same compounds could be formed also from α,α-dichloroethyltrichlorosilane (II), owing to the possibility of intramolecular rearrangement. In the case of β,β-dichloroethyltrichlorosilane (III) migration of the carbonium ion or the chlorine atom to the α-position is excluded on the basis of a critical analysis of all existing literature data on silicoalkylation and the reaction of $AlCl_3$ with chloroalkylsilane chlorides [3].

In order to determine the structure of the compounds obtained we turned to the UV absorption spectra. The spectra of the methylated reaction products were obtained with an ISP-22 quartz spectrograph by the photographic method, an Ostroumov-type hydrogen lamp being used as the source of the continuous spectrum. It is known [4] that UV spectra of compounds, in which there is an aliphatic bridge of two carbon atoms (Figure 1a) or one carbon atom (Figure 1b) between the aromatic ring and the silicon atom, exhibit a substantial difference which consists in an approximately 2-fold increase in the intensity of the principal absorption band and the displacement of the entire spectrum by about 5 mμ toward the long-wave region for the second case [cf. the 275 mμ band (Figure 1b) and the 270 mμ band (Figure 1a)]. In compounds of the $\geq SiCH_2C_6H_5$ type substitution of a methyl radical for a hydrogen atom $\left[\geq \underset{\underset{CH_3}{|}}{SiCH}C_6H_5\right]$ has practically no

TABLE 1

Experiment No.	Silicoalkylating agent	Aromatic compound	Compound obtained	Reaction time (in hr)	Yield based on original chloride (in %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}
1	$Cl_2CHSiCl_3$	C_6H_5Cl	$(ClC_6H_4)_2CHSiCl_3$ Bis(chlorophenyl)methyltrichlorosilane	64	31.2	197—198° (8)	1.5945	1.4343
2	$Cl_2CHSiCl_2CH_3$	C_6H_6	$(C_6H_5)_2CHSiCl_2CH_3$ Bis(phenyl)methylmethyldichlorosilane	40	5.6	134—135 (3)	1.5735	1.1917
3	$Cl_2CHSiCl_2CH_3$	C_6H_5Cl	$(ClC_6H_4)_2CHSiCl_2CH_3$ Bis(chlorophenyl)methylmethyldichlorosilane	40	42.3	196—197 (4.5)	1.5908	1.3383
4	$Cl_2CHSiCl_2CH_3$	$C_6H_5CH_3$	$(CH_3C_6H_4)_2CHSiCl_2CH_3$ Bis(tolyl)methylmethyldichlorosilane	50	4.1	159—163 (4)	1.5639	1.1392
5	$CH_3CCl_2SiCl_3$	C_6H_6	$CH_3C(C_6H_5)_2SiCl_3$ α,α-Diphenylethyltrichlorosilane	12	38	173 (15)	1.5845	1.3111
6	$CH_3CCl_2SiCl_3$	C_6H_5Cl	a) $CH_3CH(C_6H_4Cl)SiCl_3$ α-Chlorophenylethyltrichlorosilane	12	8.7	126—128 (3)	1.5392	1.3528
			b) $CH_3C(C_6H_4Cl)_2SiCl_3$ α,α-Bis(chlorophenyl)ethyltrichlorosilane	12	40	226—227 (5)	1.5985	1.4125
7	$CH_3CCl_2SiCl_3$	$C_6H_5CH_3$	a) $CH_3CH(C_6H_4CH_3)SiCl_3$* α-Tolylethyltrichlorosilane	40	41	96—98 (3)	1.5222	1.2271
			b) $CH_3C(C_6H_4CH_3)_2SiCl_3$ α,α-Ditolylethyltrichlorosilane	40	5.2	156—160 (3)	1.5760	1.2221
8	$Cl_2CHCH_2SiCl_3$	C_6H_6	$(C_6H_5)_2CHCH_2SiCl_3$ β,β-Diphenylethyltrichlorosilane	12	15	168—169 (6.5) M.p. 67—68° (from benzene)	—	—
9	$Cl_2CHCH_2SiCl_3$	C_6H_5Cl	$(ClC_6H_4)_2CHCH_2SiCl_3$ β,β-Bis(chlorophenyl)ethyltrichlorosilane	12	25.8	198—200 (6)	1.5830	1.3954
10	$Cl_2CHCH_2SiCl_3$	$C_6H_5CH_3$	a) $CH_3C_6H_4CH_2CH_2SiCl_3$* β-Tolylethyltrichlorosilane	12	10.7	105—106 (3)	1.5178	1.2139
			b) $(CH_3C_6H_4)_2CHCH_2SiCl_3$ β,β-Ditolylethyltrichlorosilane	12	3.1	173—174 (5) M.p. 53—54° (from benzene)	—	—
11	$ClCH_2CHClSiCl_3$	C_6H_6	a) $C_6H_5CH_2CH_2SiCl_3$ β-Phenylethyltrichlorosilane	13.5	4.2	98—99 (5) **	1.5180	1.2394
			b) $C_6H_5CH_2CH(C_6H_5)SiCl_2$ α,β-Diphenylethyltrichlorosilane	13.5	9.5	162—163 (5) M.p. 60—61° (from benzene)	—	—
12	$ClCH_2CHClSiCl_3$	C_6H_5Cl	a) $ClC_6H_4CH_2CH_2SiCl_3$ α,β-Chlorophenylethyltrichlorosilane	12	4.9	122 (5)	1.5312	1.3459
			b) $ClC_6H_4CH_2CH(C_6H_4Cl)SiCl_3$ α,β-Bis(chlorophenyl)ethyltrichlorosilane	12	27.4	207—208 (5)	1.5833	1.3971
13	$ClCH_2CHClSiCl_3$	$C_6H_5CH_3$	a) $CH_3C_6H_4CH_2CH_2SiCl_3$* β-Tolylethyltrichlorosilane	20	19.6	113—114.5 (7)	1.5178	1.2125
			b) $CH_3C_6H_4CH_2CH(C_6H_4CH_3)SiCl_3$ α,β-Ditolylethyltrichlorosilane	20	5.6	173.5—175 (7)	1.5590	1.2061

* The compound was methylated by means of CH_3MgCl, and the UV spectrum of the reaction product was taken. The properties of the compound are given in Table 2.

** Literature data: b.p. 240.5° (739 mm), n_D^{20} 1.5188, d_4^{20} 1.2395.

TABLE 1 (continued)

	MR_D		Found (in %)				Empirical formula	Calculated (in %)			
	found	calculated	C	H	Si	Cl		C	H	Si	Cl
1	87.71	87.33	41.90, 41.90	2.34, 2.41	7.50, 7.42	46.95, 47.20	$C_{13}H_9Cl_5Si$	42.06	2.54	7.54	47.86
2	77.73	78.02	59.91, 59.88	5.09, 5.04	9.73, 9.70	25.87, 25.94	$C_{14}H_{14}Cl_2Si$	59.78	5.02	9.98	25.22
3	88.35	87.70	48.26, 48.20	3.46, 3.43	8.14, 8.08	39.51, 40.02	$C_{14}H_{12}Cl_4Si$	48.02	3.43	8.02	40.53
4	88.18	87.28	62.82, 62.72	5.97, 5.90	8.51, 8.68	22.18, 22.32	$C_{16}H_{18}Cl_2Si$	62.14	5.87	9.06	22.93
5	82.72	82.28	53.40, 53.50	4.30, 4.36	8.98, 8.98	33.67, 33.45	$C_{14}H_{13}Cl_3Si$	53.25	4.15	8.90	33.70
	62.96	62.41	35.80, 35.72	2.67, 2.44	10.50, 10.52	51.27, 51.20	$C_8H_8Cl_4Si$	35.32	2.28	10.30	52.10
6	92.88	91.96	43.59, 43.62	2.89, 2.86	6.85, 6.94	45.42, 45.68	$C_{14}H_{11}Cl_5Si$	43.69	2.86	7.28	46.17
	62.99	62.67	42.94, 43.02	4.38, 4.40	10.70, 10.62	41.80, 41.55	$C_9H_{11}Cl_3Si$	42.74	4.35	10.74	42.12
7	92.97	91.54	56.55, 56.72	5.20, 5.85	7.66, 7.54	30.10, 30.25	$C_{16}H_{17}Cl_3Si$	56.00	5.00	8.03	30.97
8	—	—	53.52, 53.45	4.32, 4.36	8.98, 8.76	33.10, 33.18	$C_{14}H_{13}Cl_3Si$	53.25	4.15	8.90	33.70
9	92.09	91.96	44.00, 43.96	2.89, 2.86	7.34, 7.28	45.55, 45.75	$C_{14}H_{11}Cl_5Si$	43.69	2.86	7.28	46.17
	62.00	62.67	42.98, 43.00	4.30, 4.28	10.58, 10.55	41.75, 41.62	$C_9H_{11}Cl_3Si$	42.74	4.35	10.79	42.12
10	—	—	55.88, 55.35	5.12, 5.10	8.10, 8.12	31.69, 30.75	$C_{16}H_{17}Cl_3Si$	56.00	5.00	6.03	30.97
	58.54	58.04	—	—	—	—	$C_8H_9Cl_3Si$	—	—	—	—
11	—	—	53.20, 53.10	4.09, 4.10	8.75, 8.83	33.27, 33.12	$C_{14}H_{13}Cl_3Si$	53.25	4.15	8.90	33.70
	62.92	62.88	—	—	—	—	$C_8H_8Cl_4Si$	—	—	—	—
12	91.96	91.96	43.90, 43.86	3.10, 3.05	7.06, 7.10	45.88, 45.98	$C_{14}H_{11}Cl_5Si$	43.69	2.86	7.28	46.17
	63.20	62.87	—	—	—	—	$C_9H_{11}Cl_3Si$	—	—	—	—
13	91.90	91.54	55.81, 55.90	5.10, 5.08	7.94, 8.00	31.16, 31.32	$C_{16}H_{17}Cl_3Si$	56.00	5.00	8.03	30.97

effect on the interaction of the silicon atom and the aromatic ring. UV spectra of compounds of the $\geq SiCH_2CH_2C_6H_5$ type differ little from those of monoalkylbenzenes.

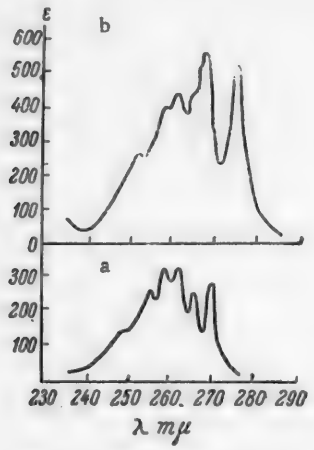

Fig. 1. Ultraviolet spectra of $C_6H_5CH_2CH_2SiR_3$ (a) and $C_6H_5CH_2SiR_3$ (b) in 2,2,4-trimethylpentane solution.

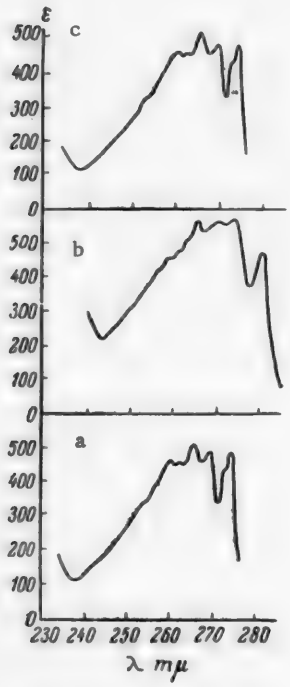

Fig. 2. Ultraviolet spectra of products of the reaction of I (a), II (b), and III (c) with toluene in 2,2,4-trimethylpentane solution.

In Figure 2a, b, c are shown UV spectra of the products of the reaction of toluene with (I), (II), and (III). Spectra a and c are identical. Therefore, in α,β-dichloroethyltrichlorosilane the β-chlorine atom is displaced by an aromatic radical and the α-chlorine atom by hydrogen. The spectrum of the product of reaction of (II) with toluene (Figure 2b) differs from the other two spectra and has the same peculiarities as that in Figure 1b. Therefore, with α,α-dichloroethyltrichlorosilane the reaction takes place, in the main, without rearrangement. However, the complex form of the 267-280 mμ band, two peaks of which (268 and 278 mμ) exactly reproduce the positions of the corresponding peaks of spectra 2a and 2c, and the increased intensity at the point of the principal minimum ($\epsilon = 220$, $\lambda = 247$ mμ instead of the usual $\epsilon \approx 100$) give grounds for assuming that in the formation of type A, insignificant amounts of type B are also formed.

On the basis of comparison of the UV spectra in Figures 2a and 2c, it may be asserted that we have mainly para-isomers in both cases. The presence of the shoulder at 272 mμ suggests that a small amount of the meta-isomer is also formed. In spectrum 2b only one long-wave maximum is observed at about 280 mμ, i.e., displaced exactly 5 mμ with respect to the p-xylene maximum. This, as well as the absence of other bands near this peak, permits the assertion that in this case only the para-isomer is formed.

EXPERIMENTAL

Dichloromethyltrichlorosilane, dichloromethylmethyldichlorosilane, and α,α-, β,β-, and α,β-dichloroethyltrichlorosilanes were prepared by the methods given in [6] and had the following properties: dichloromethyltrichlorosilane, b.p. 144° (750 mm); dichloromethylmethyldichlorosilane, b.p. 148-149° (750 mm); α,α-dichloroethyltrichlorosilane, b.p. 152-153° (750 mm), m.p. 115°; α,β-dichloroethyltrichlorosilane, b.p. 184° (750 mm); β,β-dichloroethyltrichlorosilane, b.p. 173° (750 mm).

The reaction of dichloromethyltrichlorosilane with benzene was described by us earlier [1].

Three standard procedures for conducting the reaction are given. Experimental results are given in Table 1.

1. Bis(chlorophenyl)methyltrichlorosilane. The reaction of dichloromethyltrichlorosilane with chlorobenzene was conducted in a three-neck flask provided

TABLE 2

Original compound	Compound obtained	Yield (in %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	Empirical formula	MR_D found	MR_D calculated
$CH_3CH(C_6H_4CH_3)SiCl_3$ From reaction 7 (Table 1)	$CH_3CH(C_6H_4CH_3)Si(CH_3)_3$ α-Tolylethyltrimethylsilane	70	88—89 (6)	1.4955	0.8756	$C_{12}H_{20}Si$	64.00	63.78
$CH_3C_6H_4CH_2CH_2SiCl_3$ From reaction 10 (Table 1)	$CH_3C_6H_4CH_2CH_2Si(CH_3)_3$ β-Tolylethyltrimethylsilane	73	222—224 (745)	1.4882	0.8640	$C_{12}H_{20}Si$	63.95	63.78
$CH_3C_6H_4CH_2CH_2SiCl_3$ From reaction 13 (Table 1)	$CH_3C_6H_4CH_2CH_2Si(CH_3)_3$ β-Tolylethyltrimethylsilane	78	223—224 (742)	1.4878	0.8637	$C_{12}H_{20}Si$	63.93	63.78

with a stirrer, a thermometer, and a reflux condenser. Into the flask was put 130 g of dichloromethyltrichlorosilane, 224 g of chlorobenzene, and 10 g of $AlCl_3$. The reaction mixture was heated with vigorous stirring at the boiling point of the mixture for 64 hours, after which 20 g of $POCl_3$ was added in order to form the complex $AlCl_3 \cdot POCl_3$. After cooling, the precipitate formed was filtered off, and the filtrate was distilled. On distillation 48 g of dichloromethyltrichlorosilane and 69 g of bis(chlorophenyl)methyltrichlorosilane were isolated; yield, 31.2% based on original and 49.5% based on reacted $Cl_2CHSiCl_3$. All reactions with $Cl_2CHSiCl_3$ and $Cl_2CHSiCl_2CH_3$ were conducted under similar conditions.

2. α,α-Diphenylethyltrichlorosilane. Into the apparatus of Experiment 1, provided with an additional dropping funnel, was placed 40 g of benzene and 3 g of $AlCl_3$. With vigorous stirring a mixture of 46.4 g of α,α-dichloroethyltrichlorosilane and 38 g of benzene was slowly added. The reaction began almost immediately, and HCl was vigorously evolved during the entire time of addition of the mixture. After HCl evolution ceased, the mixture was heated to 70-80° for 10 hours more. Then 6 g of $POCl_3$ and 20 ml of isooctane was added, and after cooling, the precipitate formed was filtered off. On distillation of the filtrate 23.9 g of α,α-diphenylethyltrichlorosilane was isolated. The rest of the reactions with α,α-dichloroethyltrichlorosilane and β,β-dichloroethyltrichlorosilane were conducted under the same conditions.

3. Reaction of α,β-dichloroethyltrichlorosilane and benzene. Into the apparatus of Experiment 1 was placed 35 g of α,β-dichloroethyltrichlorosilane, 78 g of benzene, and 0.3 g of aluminum powder. The mixture was heated to 85° for 3.5 hours, after which vigorous evolution of HCl began. The mixture was heated to 80-90° for 10 hours. Evolution of HCl nearly ceased. On cooling, the reaction product was distilled. One and one-half g of β-phenylethyltrichlorosilane and 4.5 g of α,β-bis(phenyl)ethyltrichlorosilane were obtained. The rest of the reactions with α,β-dichloroethyltrichlorosilane were conducted under the same conditions.

SUMMARY

1. It has been shown that silicoalkylation of benzene, toluene, and chlorobenzene by dichloroethyltrichlorosilanes is accompanied by the reduction by hydrogen of one chlorine atom in the dichloroethyl radical. In the case of benzene and chlorobenzene this is a side reaction, but in the case of toluene it has become the main reaction. In silicoalkylation by means of dichloromethylsilane chlorides reduction is not observed.

2. The UV spectra of a series of the synthesized compounds were taken after methylation of the latter; this made it possible to define the structures of these compounds more exactly.

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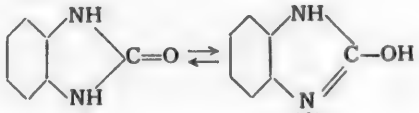
CYANOETHYLATION OF BENZIMIDAZOLONE AND MERCAPTOBENZIMIDAZOLE

A. M. Efros

Recently a great number of works [1] on the use of derivatives of urea and thiourea as herbicides and stimulators of vegetable growth have appeared in the literature. Thus it is known that N-4-chlorophenyl-N,N'--dimethylurea is used as a powerful herbicide for combating monocotyledonous weeds [2]. Chlorophenyldimethylurea and N-phenyl-N,N'-dimethylurea [3] are not inferior to this substance with respect to physiological activity. With consumption rates of 9-18 kg per hectare phenyldimethylurea is a herbicide of continuous action. Derivatives of this class of compounds, such as N-3,5-dichloro-4-methoxyphenyl-N,N'-dimethylurea and other compounds [4], are to a greater or lesser degree substances which stimulate vegetable growth, or herbicides.

Cyclic derivatives of urea and thiourea have not yet been studied in this connection. From this point of view benzimidazolone, which was studied in detail by L. S. Efros [5], may be of definite interest as a basis for the synthesis of substances having a herbicidal effect. Thus it has been shown by the investigation of ultraviolet spectra, reactivity, and basicity constants that of the two possible tautomeric forms — orthophenyleneurea (I) and 2-hydroxybenzimidazole (II) — benzimidazolone exists mainly in the first, thus being a cyclic derivative of urea.



(I) (II)

Comparison of the basicity constants and ultraviolet absorption spectra of benzimidazolone, 1,3-dimethylbenzimidazolone, and 2-ethoxybenzimidazole in neutral methanol shows that under ordinary conditions benzimidazolone exists also in the orthophenyleneurea form; benzimidazolone and its 1,3-dimethyl derivative contain a hydroxyl group in position 2, i.e., correspond to form (II), only in a strongly acid medium [6].

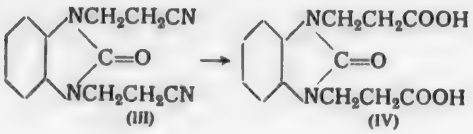
Furthermore, it was shown by a whole series of other investigations that in an alkaline medium the alkylation and benzoylation [7,8], of benzimidazolone, as well as its reaction with formaldehyde [9] and its methylation by dimethyl sulfate [10], lead to the formation of N,N'-disubstituted orthophenyleneureas. Neither the cyanoethylation of benzimidazolone nor that of mercaptobenzimidazole is described in the literature.

In the present work we decided to study the cyanoethylation of benzimidazolone and mercaptobenzimidazole in the presence of a quaternary base in order to observe the course of the reactions of the given substances with acrylonitrile and to prepare compounds which, from our point of view, must also have physiological activity. The cyanoethylation of benzimidazolone was carried out at a temperature of 40-50° in the presence of triethylbenzylammonium hydroxide as catalyst. In the absence of a catalyst or in the presence of 33% caustic alkali the cyanoethylation of benzimidazolone, as well as that of mercaptobenzimidazole, does not occur. Moreover, if the cyanoethylation is carried out between equimolar quantities of these substances, two acrylonitrile radicals invariably enter into the benzimidazolone or mercaptobenzimidazole molecule.

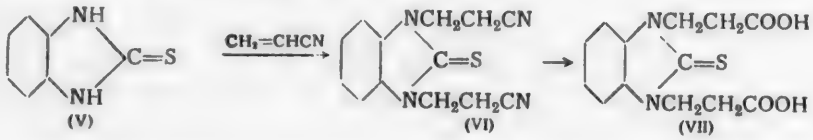
As a result of the cyanoethylation of benzimidazolone the dinitrile N,N'-dicyanoethylbenzimidazolone (III), m.p. 178-180°, was obtained in good yield.

By hydration of the dinitrile (III) with barium hydroxide in aqueous solution, the barium salt of N,N'-dicarboxyethylbenzimidazolone was obtained; on treatment of this with an equimolar quantity of 0.1 N sulfuric

acid the dibasic acid N,N'-dicarboxyethylbenzimidazolone (IV) was obtained in about 80% yield; m.p. 188-189.5°.



The cyanoethylation of mercaptobenzimidazole (V) takes place on longer heating at a higher temperature. On hydration of the dinitrile obtained, N,N'-dicyanoethylbenzimidazolethione (VI), with barium hydroxide and subsequent treatment of the barium salt with 0.1 N sulfuric acid, the dibasic acid, N,N'-dicarboxyethylbenzimidazolethione (VII), m.p. 186-187°, was obtained.



We believe that the cyanoethyl radicals are attached to the nitrogen atoms in the case of both products; however, the exact proof of this requires further investigation.

EXPERIMENTAL

Cyanoethylation of benzimidazolone. Into a three-neck flask, provided with a reflux condenser, a dropping funnel and a thermometer, were put 15 ml of dioxane, 8 g of benzimidazolone, and 0.8 g of triethylbenzylammonium hydroxide; on heating to 40-50°, 14 g (a two-fold excess) of acrylonitrile was gradually added from a dropping funnel. After the beginning of the reaction the reaction mass was heated at 40-50° for 3-4 hours. Thereupon a copious, crystalline precipitate formed, which was filtered off and dried at 105°. The technical product melted at 168-170°. A considerable quantity of the reaction product separated from the mother liquor on evaporation. The yield of N,N'-dicyanoethylbenzimidazole (III), after recrystallization from water, from acetone, and twice from alcohol, amounted to 7.8 g (55.4%). The substance was prepared for the first time.

Found %: C 64.90, 64.58; H 5.40, 5.27; N 23.24, 23.48. $C_{13}H_{12}ON_4$. Calculated %: C 65.00; H 5.00; N 23.3.

Hydrolysis of N,N'-dicyanoethylbenzimidazolone. Two g of (III), 1.4 g of barium hydroxide, and 50 ml of water were put into a two-neck flask provided with a reflux condenser and a thermometer. The solution was boiled for 2-2.5 hours, until ammonia ceased to be evolved. The precipitate was filtered off, the filtrate was saturated by a stream of carbon dioxide, and the resulting barium carbonate precipitate was filtered out of the solution. The solution was then concentrated and treated with an equimolar quantity of 0.1 N sulfuric acid. The dibasic acid dicarboxyethylbenzimidazolone (IV), which was prepared for the first time, was a white, crystalline product readily soluble in alcohol, acetone, or ether. M.p. 188-189.5° after 2-fold recrystallization from water. Yield, 90.3%.

Found %: C 55.55, 55.84; H 5.32, 4.93. M 278, 294 (by potentiometric titration). $C_{13}H_{14}O_5N_2$. Calculated %: C 55.55; H 4.89. M 278.

Cyanoethylation of mercaptobenzimidazole (V). Into a flask with a reflux condenser, a dropping funnel, and a thermometer were put 5 g of mercaptobenzimidazole, 15 ml of dioxane, and 0.5 g of triethylbenzylammonium hydroxide dissolved in 2 ml of ethyl alcohol. The mixture was heated to 50° on a water bath, and 4.5 ml (a twofold excess) of acrylonitrile was gradually added during a 3-hour period. The reaction mixture was heated to 70-75° for 4-5 hours and then poured into 50 ml of water. After 24 hours crystals of N,N'-dicyanoethylbenzimidazolethione (VI) settled out. M.p. 229-230.5° after two recrystallizations from water and then from acetone. Yield, 6 g (70.6%). The product is a white, crystalline substance readily soluble in benzene.

Found %: C 61.16, 61.15; H 4.9, 4.5; N 21.58, 21.26; S 11.87, 11.86. $C_{13}H_{12}N_4S$. Calculated %: C 60.93; H 4.68; N 21.87; S 12.3.

Hydrolysis of N,N'-dicyanoethylbenzimidazolethione (VI). The reaction products were hydrolyzed and worked up under the conditions described above. The dibasic acid obtained, N,N'-dicarboxyethylbenzimidazolethione (VII), is readily soluble in alcohol and in water. The acid was recrystallized twice from acetone and petroleum ether, and it melted at a temperature of 186-187°.

Found: M 302 (by potentiometric titration). $C_{13}H_{14}O_4N_2S$. Calculated: M 294.

SUMMARY

1. N,N'-dicyanoethylbenzimidazolone and N,N'-dicyanoethylbenzimidazolethione have been prepared by cyanoethylation of benzimidazolone and mercaptobenzimidazole, respectively, in the presence of triethylbenzylammonium hydroxide.

2. By hydrolysis of the resulting dinitriles in the presence of barium hydroxide, dicarboxyethylbenzimidazolone and dicarboxyethylbenzimidazolethione were prepared for the first time.

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CHEMISTRY OF SELENOPHENE

X. SYNTHESIS OF 3-METHYLSELENOPHENE-2-ALDEHYDE AND 2,3- AND 2,4-DIMETHYLSELENOPHENE

Iu. K. Iur'ev, N. K. Sadovaia, and M. A. Gal'bershtam

In the works of Umezawa [1,2] reactions of substitution in the selenophene ring, exemplified by the halogenation, nitration, sulfation, acylation, and mercuration of selenophene, were studied. It follows from these works that with selenophene, as well as its isologs, furan and thiophene, the place of entrance of the second substituent into the ring is determined not only by the nature of the substituent already present and the nature of the second substituent entering the ring, but also to a very considerable degree by the nature of the hetero-atom.

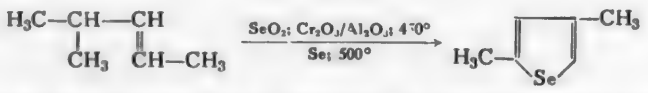
Thus, when a substituent of the first kind, e.g., halogen, is present in position 2 of the selenophene ring, the second substituent (halogen or a nitro group) enters in position 5. If there is a substituent of the second kind (nitro or sulfonyl chloride group) in position 2, the second substituent, e.g., a nitro group, as in the nitration of 2-nitrothiophene, enters positions 4 and 5 in the ring simultaneously to form the isomeric 2,4- and 2,5-dinitroselenophenes, but with predominance of the 2,4-isomer. When a nitro group is present in position 3, the second nitro group enters in position 5.

On conducting the iodination and metalation of the selenophene ring in 3-methylselenophene and 2,4-dimethylselenophene [3], considering that the similarity in structure of selenophene and thiophene must make for close similarity in their chemical properties, we assumed a priori that on replacement of hydrogen by iodine in 3-methylselenophene, 2-iodo-3-methylselenophene is formed; the latter, on subsequent metalation with phenyllithium and carboxylation, gives 3-methylselenophene-2-carboxylic acid. On the same basis we assumed that in the iodination of 2,4-dimethylselenophene replacement of hydrogen by iodine occurs in position 5 of the ring with formation of 5-iodo-2,4-dimethylselenophene, and therefore we assigned the structure of 2,4-dimethylselenophene-5-carboxylic acid to the product of subsequent metalation and carboxylation of the former.

However, it was necessary to prove, firstly, that when there is a methyl group in position 3 of the selenophene ring, halogenation, and also mercuration, actually takes place in position 2, and secondly, that in the case of 2,4-dimethylselenophene these substitution reactions take place in position 5.

In the present work conclusive proofs of the correctness of the orientation of 3-methyl- and 2,4-dimethylselenophene, assumed by us, in the reactions of iodination and mercuration are adduced.

For the preparation of 2,4-dimethylselenophene we used 2-methylpentene-3, which was brought into reaction with selenium dioxide in the presence of chromic oxide on aluminum oxide [4], and also into reaction with metallic selenium [5].



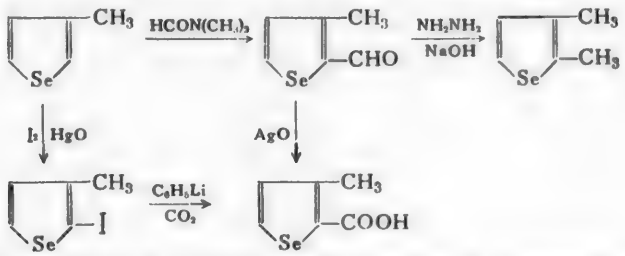
It is evident from the given scheme that on dehydration of 2-methylpentene-3 and ring closure by reaction with selenium [6], either formed from selenium dioxide in the first stage of this process or introduced into the reactor beforehand, only 2,4-dimethylselenophene could be obtained.

For the preparation of 2,3-dimethylselenophene we used 3-methylselenophene; on formylation of the latter by a method developed by one of us [7], we obtained an aldehyde and assigned to it the structure of 3-methylselenophene-2-aldehyde (yield 72%); on reduction of this aldehyde by the usual Kizhner procedure [8] and the method described for the reduction of selenophene-2-aldehyde [7], we accordingly obtained 2,3-dimethylselenophene. Proofs of the correctness of the structures assigned by us to the product of formylation of 3-methylselenophene and the product of subsequent reduction of the aldehyde obtained consist of the following: 1) 2,3-dimethylselenophene differed in its constants (b.p. 159.5-160° at 756 mm, $n^{20}D$ 1.5539, d^{20}_4 1.3734) from 2,4-dimethylselenophene (b.p. 159.5-160° at 746 mm, $n^{20}D$ 1.5498, d^{20}_4 1.3672), described in the present work; 2) the melting point of the chloromercuric derivative of 2,3-dimethylselenophene (~240° with decomp.) sharply differed from that of the chloromercuric derivative of 2,4-dimethylselenophene (155-156°), and a mixture test of them showed a depression (m.p. 145°).

Thus there is no doubt that in the formylation of 3-methylselenophene, 3-methylselenophene-2-aldehyde is obtained, and therefore substitution takes place in position 2.

In order to prove that in the halogenation of 3-methylselenophene halogen replaces hydrogen in position 2, we carried out the oxidation of 3-methylselenophene-2-aldehyde with silver oxide in an alkaline medium and obtained an acid which was 3-methylselenophene-2-carboxylic acid, identical with the acid obtained by us earlier through metalation and subsequent carboxylation of the iodine derivative of 3-methylselenophene [3]: a mixture test-sample of these acids melted without depression.

Thus, in the reactions of halogenation, mercuration, and formylation of 3-methylselenophene, studied by us, displacement of hydrogen situated in position 2 of the selenophene ring takes place.



By reduction of 3-methylselenophene-2-aldehyde with formaldehyde in an alkaline medium we obtained 3-methylselenophene-2-carbinol.

The preparation of isomeric dimethylselenophenes was accomplished through the syntheses of 2,3- and 2,4-dimethylselenophenes, described in the present work.

EXPERIMENTAL

2,4-Dimethylselenophene. a) In accordance with the method of one of us [4], a mixture of 25 g of 2-methylpentene-3 (b.p. 57-58° at 755 mm, $n^{20}D$ 1.3892, d^{20}_4 0.6731) and sublimed selenium dioxide (30 g) was passed over chromic oxide on aluminum oxide in a current of nitrogen at 450° at a space velocity of 0.5 ml of hydrocarbon per ml of catalyst per hour. The catalyzate obtained was washed with water and caustic soda solution and dried with fused caustic potash. On distillation of the reaction product there were isolated 13 g of unchanged 2-methylpentene-3 (52%) and 5.6 g of 2,4-dimethylselenophene (23%, calculated on the basis of reacted hydrocarbon):(b.p. 155-159° at 740 mm, $n^{20}D$ 1.5482, d^{20}_4 1.3639).

b) Fifty g of finely ground selenium was mixed with small pieces of porcelain, put into a silica tube, and heated to 500° [5]. Seventeen g of 2-methylpentene-3 was passed through the tube at a rate of 0.5 ml/min in a slow current of nitrogen. The catalyzate obtained was treated as described above. On distillation of the reaction product there were isolated 8.4 g of unchanged 2-methylpentene-3 (50%) and 3.8 g of 2,4-dimethylselenophene (23.5%, calculated on the basis of reacted hydrocarbon): (b.p. 157-161° at 760 mm, $n^{20}D$ 1.5490, d^{20}_4 1.3680).

The 2,4-dimethylselenophene obtained from a series of experiments was combined and, after distillation in a column (18 theoretical plates), had the following constants:

B.p. 159.5-160° (746 mm), $n^{20}D$ 1.5498, d^{20}_4 1.3672, MR_D 37.07. C_6H_8Se. Calculated MR_D 37.38.

Found %: C 45.74, 45.81; H 5.14, 5.21. C_6H_8Se. Calculated %: C 45.29; H 5.07.

2,4-Dimethyl-5-chloromercuriselenophene, obtained by the reaction of 2,4-dimethylselenophene with mercuric chloride in aqueous-alcoholic solution in the presence of sodium acetate, melted at 155-156° (from alcohol).

Found %: Hg 50.68, 50.81. $C_6H_7ClHgSe$. Calculated %: Hg 50.84.

3-Methylselenophene-2-aldehyde. Into a three-neck flask with a stirrer, a dropping funnel, and a reflux condenser were put 29.4 g (0.2 mole) of 3-methylselenophene and 18.7 g (0.26 mole) of dimethylformamide, and 39.6 g (0.26 mole) of phosphorus oxychloride was gradually added, the mixture being cooled from time to time with ice water. This was followed by heating for 1 hour at 50-70°, cooling to 20°, and pouring into a mixture of 500 g of ice and 400 g of sodium acetate, with stirring. When the ice melted, the mixture was carefully heated to boiling and cooled, the oil layer was drawn off, the water layer was extracted three times with ether, and the extracts were combined with the oil layer. After drying with anhydrous magnesium sulfate, driving off the ether, and distillation, 25 g (72%) of 3-methylselenophene-2-aldehyde was obtained:

B.p. 111° (12 mm), $n^{20}D$ 1.6198, d^{20}_4 1.5602, MR_D 38.93. C_6H_6OSe. Calculated MR_D 37.39; EM_D + + 1.54.

Found %: C 41.66, 41.88; H 3.64, 3.66. C_6H_6OSe. Calculated %: C 41.64; H 3.49.

3-Methylselenophene-2-aldehyde semicarbazone: m.p. 202-202.5° (from 50% alcohol).

Found %: N 18.56, 18.44. $C_7H_9ON_3Se$. Calculated %: N 18.26.

3-Methylselenophene-2-aldehyde thiosemicarbazone: m.p. 197° (from alcohol).

Found %: N 16.85, 17.14. $C_7H_9N_3SSe$. Calculated %: N 17.06.

3-Methylselenophene-2-aldehyde 2,4-dinitrophenylhydrazone: m.p. 212-213° (from a mixture of ethyl alcohol and ethyl acetate).

Found %: N 15.82, 15.76. $C_{12}H_{10}O_4N_4Se$. Calculated %: N 15.86.

3-Methylselenophene-2-carboxylic acid. To an aqueous-alcoholic solution of 0.5 g of 3-methylselenophene-2-aldehyde and 1 g of silver nitrate was gradually added 0.3 g of caustic soda in 18 ml of water, with stirring. After standing for a day the silver hydroxide was filtered off, and the filtrate was concentrated, acidified with concentrated sulfuric acid, and extracted with ether. After evaporation of the ether 0.4 g (74%) of 3-methylselenophene-2-carboxylic acid was obtained; m.p. 133-134° (from water). A mixture test with 3-methylselenophene-2-carboxylic acid, obtained from 2-iodo-3-methylselenophene, [3], showed no depression; m.p. 133°.

3-Methylselenophene-2-carbinol. Into a flask with a stirrer, a reflux condenser, a dropping funnel, and a thermometer were put 10.4 g (0.06 mole) of 3-methylselenophene-2-aldehyde, 10 ml of 40% formalin, and 20 ml of anhydrous methyl alcohol. The mixture was heated to 65°, and a solution of 11 g of caustic soda in 10 ml of water was quickly added, the flask being cooled with ice water in order to keep the temperature from exceeding 65°. The mixture was then heated for one-half hour at 60-70°, cooled to 20°, poured on to ice, and extracted three times with benzene; the extracts were washed with 2 N hydrochloric acid and water and dried with anhydrous magnesium sulfate. After driving off the benzene 6.2 g (60%) of 3-methylselenophene-2--carbinol was obtained:

B.p. 116-117° (11 mm), $n^{20}D$ 1.5932, d^{20}_4 1.5401, MR_D 38.53. C_6H_8OSe. Calculated MR_D 38.90.

Found %: C 41.20, 41.18; H 4.53, 4.62. C_6H_8OSe. Calculated %: C 41.16; H 4.61.

3-Methylselenophene-2-carbinol α-naphthylurethane, obtained by reaction with α-naphthyl isocyanate, melted at 108-109° (from petroleum ether).

Found %: N 3.81, 3.72. $C_{17}H_{15}O_2NSe$. Calculated %: N 4.06.

2,3-Dimethylselenophene. Into a flask with a reflux condenser were put 22 g (0.13 mole) of 3-methylselenophene-2-aldehyde, 25 ml (0.5 mole) of hydrazine hydrate, 15.3 g (0.37 mole) of powdered caustic soda, and 150 ml of diethylene glycol, and the mixture was heated for one-half hour at 130° and then for 1 hour at 180°. The reflux condenser was replaced by a descending one, and everything that passed over up to 180° was distilled off. The distillate obtained was extracted with ether, and the extracts were washed with 2 N hydrochloric acid and dried with calcium chloride. After driving off the solvent and distilling the residue 17.4 g (86%) of 2,3-dimethylselenophene was obtained:

B.p. 159.5-160° (756 mm), $n^{20}D$ 1.5539, d^{20}_4 1.3734, MR_D 37.16. C_6H_8Se. Calculated MR_D 37.38.

Found %: C 45.42, 45.35; H 5.30, 5.26; Se 49.07, 48.88. C_6H_8Se. Calculated %: C 45.29; H 5.07; Se 49.08.

2,3-Dimethyl-5-chloromercuriselenophene, obtained by the reaction of 2,3-dimethylselenophene with mercuric chloride in aqueous-alcoholic solution in the presence of sodium acetate, melted ~240° with decomposition.

Found %: Hg 50.68, 50.79. $C_6H_7ClHgSe$. Calculated %: Hg 50.84.

A test-sample of a mixture with 2,4-dimethyl-5-chloromercuriselenophene melted at 145°.

Mercuration of 3-methylselenophene. To 1.5 g of 3-methylselenophene, 6.6 ml of alcohol, 3.3 g of sodium acetate, and 6.6 ml of water was added a solution of 3.2 g of mercuric chloride in 40 ml of water with slow agitation, and the mixture was stirred for 6 hours. The white precipitate was filtered off, washed with water, and extracted three times with boiling alcohol (100 ml). On cooling the alcoholic solution 2.8 g (74%) of 3-methyl-2-chloromercuriselenophene was obtained; m.p. 128-129° (from alcohol).

Found %: Hg 52.74, 52.69. $C_5H_5ClHgSe$. Calculated %: Hg 52.76.

The insoluble residue was 3-methyl-2,5-dichloromercuriselenophene; it decomposed on heating.

Found %: Hg 64.82, 64.96. $C_5H_4Cl_2Hg_2Se$. Calculated %: Hg 65.21.

SUMMARY

In the formylation, halogenation, and mercuration of 3-methylselenophene the hydrogen in position 2 of the selenophene ring is displaced.

Formylation of 3-methylselenophene by dimethylformamide leads to 3-methylselenophene-2-aldehyde, which on oxidation gives 3-methylselenophene-2-carboxylic acid and on reduction, 3-methylselenophene-2--carbinol.

Reduction of 3-methylselenophene-2-aldehyde hydrazone leads to 2,3-dimethylselenophene.

The reaction of 2-methylpentene-3 with selenium dioxide in the presence of chromic oxide on aluminum oxide, and also with metallic selenium, leads to 2,4-dimethylselenophene.

With the syntheses of 2,3- and 2,4-dimethylselenophene the preparation of isomeric dimethylselenophenes has been accomplished.

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CONVERSION OF ALLYLBENZENE OVER ALUMINOSILICATE CATALYSTS

I. STUDY OF CONVERSION KINETICS.

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In order to understand the complex processes of conversion of hydrocarbons over aluminosilicates at cracking temperatures, it is first necessary to attempt to study the mechanism of the individual stages of the process under conditions which exclude cracking, as was done in one of the preceding works [1]. In this work the kinetics of isomerization of cyclohexene was studied, and the hypothesis was advanced that the isomerization reaction takes place on active centers of two types – free aluminum oxide and aluminosilicate centers which consist of a chemical compound of the aluminosilicic acid type.

The present investigation is a continuation of work on the study of the mechanism of isomerization reactions of hydrocarbons and a check on the correctness of the expressed point of view on the effect of the two types of active centers on isomerization. For this purpose the kinetics of conversion of an aromatic hydrocarbon with an unsaturated bond in the side-chain – allylbenzene – in the liquid and vapor phases was studied, under conditions which excluded cracking, over aluminosilicate catalysts of varied composition and the initial oxides. The choice of this reaction was favorable also because, as preliminary experiments showed, we were in a position to observe not only the regularities of the isomerization reaction, but also the reactions of di- and polymerization of allylbenzene.

EXPERIMENTAL AND DISCUSSION OF RESULTS

Aluminosilicate catalysts were prepared by mixing freshly precipitated aluminum hydroxide [alumogel] and silica gels [2]. The catalysts were selectively poisoned by the method of exchange adsorption of sodium ions from aqueous sodium acetate solutions [3-5]. The surfaces and structural characteristics of the catalysts obtained were investigated by the adsorption method in a vacuum apparatus of the McBain-balance type, by taking sorption isotherms of methyl alcohol vapor. The surfaces and structural characteristics (volume of micro- and macropores, total porosity) of the poisoned catalyst specimens differed not more than 10% from those of the original catalyst specimens.

Allylbenzene was synthesized according to the method of Tiffeneau [6] by treatment of phenylmagnesium bromide with allyl chloride and purified by distillation over sodium through a rectification column having 40 theoretical plates:

B.p. 156-157° (757 mm), $n^{20}D$ 1.5130, d^{20}_4 0.8921, MR_D 39.85; calculated. 39.68.

Literature data [7]: b.p. 156-157° (758 mm), $n^{20}D$ 1.5135, d^{20}_4 0.8923, MR_D 39.50.

The study of the kinetics of conversion of allylbenzene over aluminosilicates and the original oxides was carried out in the liquid phase at 157° and in the gas phase over aluminum oxide in the temperature interval 180-250°. The experiments in the liquid phase were conducted in a special, round-bottomed flask provided with a mechanical stirrer, thermostating equipment, and a reflux condenser. The catalyzate obtained was fractionally distilled. The monomeric fraction distilled at normal pressure in the temperature interval 157-176° and was refractometrically analyzed for its allylbenzene and propenylbenzene content [8]. The presence of possible admixtures of other reaction products was checked spectroscopically by taking Raman spectra.* The

*E.G. Treshcheva took the Raman spectra, for which we thank her sincerely.

following fraction distilled at 208-210° (10 mm). Hereafter this fraction will be called the dimer on the basis of data obtained by us in the determination of the composition and structure of the compound.* The amount of the polymer was determined from the residue in the flask; we did not investigate the polymer or determine its structure.

In the study of the kinetics of conversion of allylbenzene in the liquid phase over the original oxides it was noted that on contact of allylbenzene with aluminum oxide, only isomerization of allylbenzene to propenylbenzene occurs. Silica is inactive under the given conditions.

In the study of the kinetics of conversion of allylbenzene over aluminosilicates it was established that under the given conditions the following reactions occur: shifting of the double bond in the side-chain, structural isomerization, and higher degrees of polymerization.

TABLE 1

Quantity of Catalyst, 6.3 cm^3; Duration of Experiment, 4 Hours

Composition of catalyst (in %)**		Products of conversion of allylbenzene (in %)			Total percent of conversion	Composition of catalyst (in %)**		Products of conversion of allylbenzene (in %)			Total percent of conversion
Al_2O_3	SiO_2	propenylbenzene	dimer	polymer		Al_2O_3	SiO_2	propenylbenzene	dimer	polymer	
Temperature 20°						Temperature 100°					
100	0	—	—	—	0	100	0	—	—	—	0
80	20	—	—	—	0	80	20	17	—	—	17
50	50	—	—	—	0	50	50	20	—	—	20
30	70	3	—	—	3	30	70	68	—	—	68
16	84	—	—	—	0	16	84	13	—	—	13
Temperature 50°						Temperature 157°					
100	0	—	—	—	0	100	0	20	—	—	20
80	20	5	—	—	5	80	20	3	60	37	100
50	50	5	—	—	5	50	50	2	52	45	99
30	70	6	—	—	6	30	70	2	78	20	100
16	84	5	—	—	5	16	84	2	60	20	82

In Figures 1-4 is shown the kinetics of conversion of allylbenzene over aluminosilicate catalysts of varied composition; the contact time is plotted along the horizontal axis, and the percent conversion, along the vertical axis.

On comparison of the results obtained with catalysts of compositions 16/84 and 30/70, an analogy is observed in the course of the curves for the yields of reaction products. Thus the curve of propenylbenzene yield over a catalyst of composition 16/84 passes through a pronounced maximum, as does that for a catalyst of composition 30/70 (Figures 1 and 2). The curve of polymer yield has a very pronounced maximum in both cases, while the dimer yield increases with increase of contact time. The overall course of the curves formally corresponds to the course of kinetic curves for consecutive reactions in which the intermediate products are propenylbenzene and a polymer. A different picture is obtained with catalysts containing a high percentage of aluminum oxide in their composition (Figures 3 and 4).

On comparison of the results obtained with catalysts of compositions 50/50 and 80/20, containing aluminum oxide in excess, an analogy is observed in the course of the yield curves of propenylbenzene, the dimer, and the polymer for this pair of catalysts. In this case, however, in contrast to the first pair of catalysts

*The structure and mechanism of formation of the dimer will be reported in the next article.

**Hereafter, for brevity, the composition of the catalysts will be denoted by a fraction with the percentage of aluminum oxide in the numerator and the percentage of silica in the denominator (16/84, 30/70, 50/50, and 80/20, respectively).

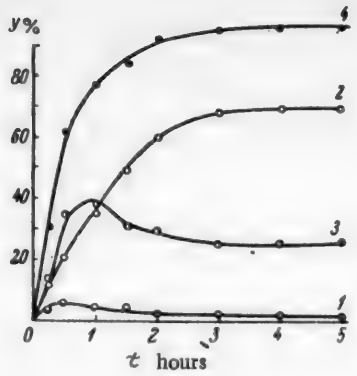

Fig. 1. Kinetics of conversion of allylbenzene over a catalyst of composition 16/84.
1) Propenylbenzene, 2) dimer, 3) polymer, 4) total percentage of conversion.

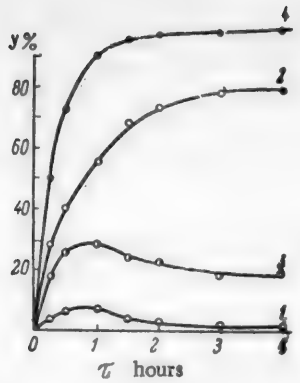

Fig. 2. Kinetics of conversion of allylbenzene over a catalyst of composition 30/70.
1) Propenylbenzene, 2) dimer, 3) polymer, 4) total percentage of conversion.

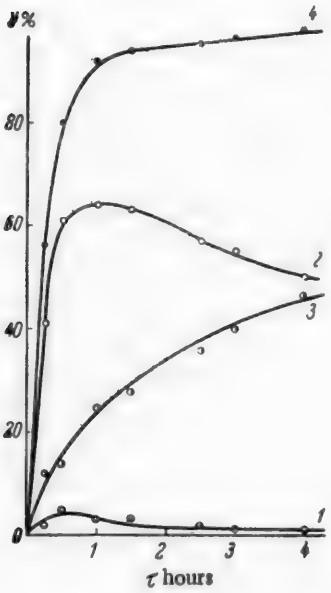

Fig. 3. Kinetics of conversion of allylbenzene over a catalyst of composition 50/50.
1) Propenylbenzene, 2) dimer, 3) polymer, 4) total percentage of conversion.

(16/84 and 30/70), the intermediate reaction products are propenylbenzene and the dimer. This sharp difference in the effect of aluminosilicate catalysts of the stated compositions, as it seems to us, is due to different relative concentrations of active centers (aluminum oxide and aluminosilicate) and the different roles of these centers in isomerization and polymerization. A sharp change in the concentration ratio of the different active centers (aluminum oxide

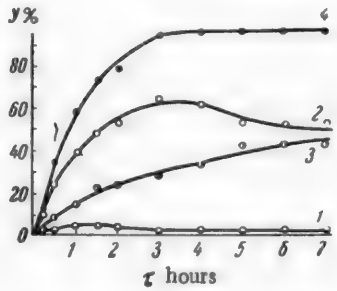

Fig. 4. Kinetics of conversion of allylbenzene over a catalyst of composition 80/20.
1) Propenylbenzene, 2) dimer, 3) polymer, 4) total percentage of conversion.

and aluminosilicate in the given case) leads to a change in the course of the kinetic curves, established in the present work.

On the basis of the data obtained on the kinetics of conversion of allylbenzene with aluminosilicate catalysts of varying aluminum oxide content, the following two schemes of the course of the reaction may be given:

(I) $C_6H_5-CH_2-CH=CH_2 \xrightarrow[Al-Si]{Al_2O_3} C_6H_5-CH=CH-CH_3 \longrightarrow$

$\longrightarrow C_6H_5-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-\underset{\underset{CH_3}{|}}{CH}-C_6H_5 \rightleftarrows$ polymer

(II) $C_6H_5-CH_2-CH=CH_2 \xrightarrow{Al-Si}$ polymer $\rightleftarrows C_6H_5-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-\underset{\underset{CH_3}{|}}{CH}-C_6H_5$.

The first scheme represents the process of conversion of allylbenzene over the 50/50 and 80/20 catalysts, and the second represents its conversion over the 16/84 and 30/70 catalysts.

The total effect of these reactions depends on the relative concentrations of the different active centers.

When the aluminum oxide content of the catalyst is greater, the reaction goes mainly according to scheme (I); i.e., allylbenzene is isomerized to propenylbenzene on the aluminum oxide and aluminosilicate active centers and then structurally isomerized and converted to the dimer and finally to the polymer on the aluminosilicate centers. If we have a catalyst with a high concentration of aluminosilicate centers and a low content of free aluminum oxide (30/70 and 16/84), the allylbenzene is converted on the aluminosilicate centers to the polymer, which then depolymerizes to form the dimer (scheme II). The occurrence of depolymerization with dimer formation was confirmed by experiments in which the polymer was boiled with the catalyst (Table 2) and by experiments in which the polymer yield was observed to decrease as the temperature increased (Figure 5).

TABLE 2

Experiments in Depolymerization (10 g of Polymer)

Catalyst composition Al_2O_3/SiO_2 (in %)	Quantity of dimer obtained (in %)	Constants of dimer*			
		boiling point	n_D^{20}	d_4^{20}	M
16/84	33	302—304°	1.5686	1.0021	236
30/70	40	302—304	1.5687	1.0022	236

In the literature there are certain works [9-14] on the polymerization of olefin hydrocarbons under the influence of floridin, in which it is stated that depolymerization of the polymeric reaction products occurs under certain conditions.

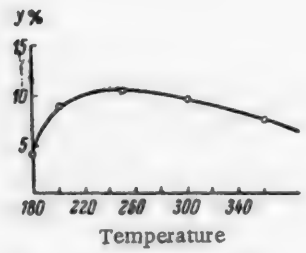

Fig. 5. Dependence of the conversion of allylbenzene to a polymer on the temperature. Catalyst of composition 16/84.

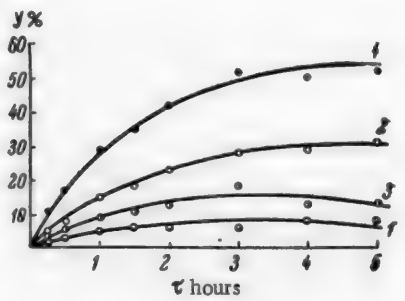

Fig. 6. Kinetics of conversion of allylbenzene over a catalyst of composition 16/84, poisoned by sodium ions (21.8 meq of Na/100 g). 1) Propenylbenzene, 2) dimer, 3) polymer, 4) total percentage of conversion.

* The constants of the dimer coincide with those of the dimer obtained from allylbenzene: b.p. 302-304°, $n^{20}D$ 1.5686, d^{20}_4 1.0023, M 236.

The possibility of depolymerization in our case becomes obvious on comparison of the kinetic data (Figures 1 and 2) obtained with catalysts containing more aluminosilicate centers than free aluminum oxide ones. It is evident from Figures 1 and 2 that under the given reaction conditions the polymer is an intermediate compound, and the polymer obviously depolymerizes to the dimer, since the yield of dimer increases as the contact time increases. The data obtained indicate that polymerization and depolymerization reactions are associated with aluminosilicate centers, and apparently the latter are alone responsible for the given reactions.

In order to confirm the above, experiments were conducted on the selective poisoning of aluminosilicate catalysts of compositions 16/84 and 50/50 by sodium ions from aqueous solutions of salts [1,3-5]. Treatment of the catalyst with an aqueous solution of sodium salts permits elimination of the aluminosilicate centers from the field of reaction without thereby affecting the free aluminum oxide.

Results obtained with catalysts partially poisoned by sodium ions (Figures 6 – 8) agree with the hypothesis of simultaneous occurrence of the two processes on different centers. From comparison of Figures 6, 7 and 8 with Figures 1 and 2 it is evident that the total percentage of conversion of allylbenzene over a poisoned specimen of composition 16/84, containing 21.8 meq of Na/100 g, was diminished 43-44%; with a specimen con-

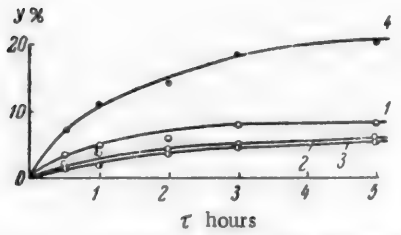

Fig. 7. Kinetics of conversion of allylbenzene over a catalyst of composition 16/84, poisoned by sodium ions (41.7 meq of Na/100 g).
1) Propenylbenzene, 2) dimer, 3) polymer, 4) total percentage of conversion.

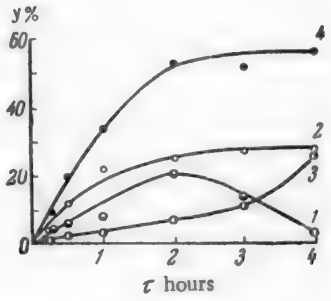

Fig. 8. Kinetics of conversion of allylbenzene over a catalyst of composition 50/50, poisoned by sodium ions (14.4 meq of Na/100 g).
1) Propenylbenzene, 2) dimer, 3) polymer, 4) total percentage of conversion.

taining 41.7 meq of Na/100 g the total percentage of conversion was lowered 80%. The yield of propenylbenzene reached 8%, while for the unpoisoned catalyst it amounted only to 2-3%. The yield of polymer was decreased considerably – 22% for a catalyst containing 21.8 meq of Na/100 g and 32% for one containing 41.7 meq of Na/100 g. For poisoned specimens the maximum on the curve was shifted in the direction of longer contact time. For a catalyst containing 21.8 meq of Na/100 g, the yield of dimer was diminished 38%. For one containing 41.7 meq of Na/100 g, the dimer yield was decreased 63%. An analogous regularity in the decrease of the dimer and polymer yields and the total percentage of conversion was also observed for a catalyst of composition 50/50, poisoned by sodium ions (Figure 8).

From the data given above, it may be concluded that dimerization and polymerization reactions take place only on aluminosilicate centers. Isomerization due to shifting of the double bond in the side-chain takes place both on aluminum oxide centers and on aluminosilicate ones; these reactions go at lower temperatures over aluminosilicate catalysts (Table 1).

On study of the data obtained it becomes obvious that in the case of partial poisoning of the aluminosilicate catalyst the rate of formation of propenylbenzene becomes commensurate with the rates of formation of the dimer and polymer. Over unpoisoned aluminosilicate catalysts the rate of formation of propenylbenzene was quite high; therefore the rate-determining step of the process in this case was the formation of the dimer and polymer.

The study of the kinetics of conversion of allylbenzene in the vapor phase in contact with aluminum oxide was carried out at 180, 200 and 250°. The isomerization of allylbenzene at the stated temperatures

over an "alumina-chromia" [alumochrome] catalyst was studied in detail by R.Ia. Levina and co-workers [6, 15, 16], and it was shown that allylbenzene is converted to propenylbenzene under these conditions.

As was shown by our experiments, which were conducted in the vapor phase by the method described earlier [1], under the studied conditions, also, allylbenzene is converted only to propenylbenzene; i.e., the reactions of redistribution of hydrogen, dimerization, and polymerization do not take place on contact with aluminum oxide at higher temperatures.

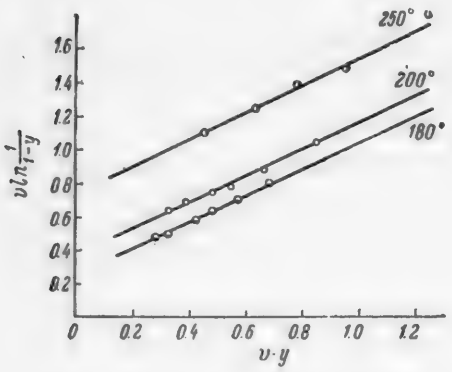

Fig. 9. Kinetics of conversion of allylbenzene over aluminum oxide in vapor phase.

The kinetics of isomerization of allylbenzene in the vapor phase over aluminum oxide (Figure 9), was studied by us, and it was shown that it is described by the equation for a unimolecular heterogeneous-catalytic reaction, in which the reaction products are sorbed more strongly than the molecules of the original substance [17].

$$v \ln \frac{1}{1-y} = \alpha + \beta v y,$$

where v is the rate of input of the original substance, y is the degree of conversion, β is a constant, and α is the apparent reaction rate.

The activation energy, calculated from kinetic data, amounts to 7300 cal/mole. The relatively low activation energy indicates the ease with which isomerization, due to shifting of the double bond in the side-chain of the aromatic hydrocarbon, takes place.

SUMMARY

1. The kinetics of conversion of allylbenzene in the liquid phase over synthetic aluminosilicate catalysts and pure aluminum oxide has been studied.

2. On contact of allylbenzene with aluminosilicate catalysts there occurs not only isomerization due to shifting of the double bond in the side-chain, but also more profound conversions of the original hydrocarbon with formation of the dimer and polymer.

3. Active centers of aluminum oxide in aluminosilicate catalysts lead only to isomerization due to shifting of the double bond in the side-chain. Aluminosilicate centers catalyze the reactions of isomerization, di-, and polymerization. The expressed point of view is confirmed by experiments on the selective poisoning of the active centers of the catalyst.

4. The stepwise mechanism of the conversion of allylbenzene over aluminosilicate catalysts has been established. The difference in the courses of conversion of allylbenzene over catalysts, which differ sharply in their percentage of free aluminum oxide, has been noted.

5. The applicability of the equation for a unimolecular heterogeneous-catalytic reaction in a stream, where the reaction products are sorbed more strongly than the original substances, to the reaction of isomerization of allylbenzene over aluminum oxide in the vapor phase has been shown.

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CONVERSION OF ALLYLBENZENE OVER ALUMINOSILICATE CATALYSTS

II. STRUCTURE AND MECHANISM OF FORMATION OF THE DIMER

K. V. Topchieva, A. I. Pletiushkina and V. A. Tronova

In the preceding work [1] the results of study of the kinetics of conversion of allylbenzene in the liquid phase over aluminum oxide and over aluminosilicate catalysts of diverse compositions were set forth. It was shown that on contact of allylbenzene with aluminum oxide, only isomerization due to shifting of the double bond in the side-chain occurs [2]. Over aluminosilicate catalysts the course of the conversion is far more complex; the reaction products are propenylbenzene, a dimer, and a polymer. The sharp difference between the course of the kinetic curves for catalysts composed of 16% Al_2O_3 and 84% SiO_2, and also 30% Al_2O_3 and 70% SiO_2, and the course of the kinetic curves obtained for catalysts containing a high percentage of aluminum oxide: 50% Al_2O_3 and 50% SiO_2, as well as 80% Al_2O_3 and 20% SiO_2, was also noted. Such a sharp difference in the effects of catalysts of the stated compositions is due to redistribution of the concentration of active centers and their different role in isomerization, dimerization and polymerization.

In the present report are given proofs of the structure and mechanism of formation of the dimer obtained from allylbenzene.

EXPERIMENTAL

The dimer obtained from allylbenzene is an oily, fluorescent liquid:

B.p. 208-210° (10 mm), 302-304° (757 mm), $n^{20}D$ 1.5686, d^{20}_4 1.0023, MR_D 77.60; calculated 78.10; M (cryoscopically) 236, 236.5. $C_{18}H_{20}$; calculated 236.

Found %: C 91.57, 91.58; H 8.28, 8.37. $C_{18}H_{20}$. Calculated %: C 91.47; H 8.53.

At reduced temperatures from -23 to -78° the dimer congeals to the amorphous state. It is readily soluble in organic solvents – benzene, ether, acetone, chloroform, carbon tetrachloride and alcohol; it decolorizes potassium permanganate and bromine water.

The structure of the hydrocarbon was proved by two methods—ozonization and oxidation with potassium permanganate in the cold. After ozonization a ketone and an aldehyde were isolated; the aldehyde was isolated through the dimedon derivative [3]; the ketone, in the form of a semicarbazone, m.p. 198° (from alcohol), and a 2,4-dinitrophenylhydrazone, m.p. 249°.

Literature data for acetophenone [4]: semicarbazone, m.p. 197-198°; 2,4-dinitrophenylhydrazone, m.p. 249-250° [4].

A mixture test of the semicarbazones showed no depression; m.p. 198°.

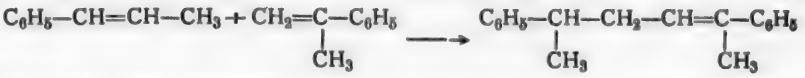
Thus the ketone isolated on ozonization of the dimer was acetophenone. The structure of the aldehyde obtained (through the dimedon derivative) could not be ascertained.

By oxidation of the dimer with potassium permanganate in the cold two acids were obtained—benzoic acid, m.p. 121° (literature data [5]: m.p. 121°); a mixture test with known benzoic acid gave no depression. The second acid, apparently, was β-phenylbutyric or β-phenylisobutyric acid: m.p. 38°, b.p. 272° (752 mm). Equivalent weight, 164 (calculated for $C_{10}H_{12}O_2$, 164). Literature data [6]: m.p. 38°, b.p. 272°.

On the basis of the data obtained by us the structure of 2,5-diphenylhexene-2 may be assigned to the unsaturated hydrocarbon. It may be assumed that it is formed as a result of one of the following reactions.

1. Dimerization of α-methylstyrene molecules formed as a result of possible isomerization of propenylbenzene.

2. Condensation of propenylbenzene molecules and already-formed α-methylstyrene molecules.



3. Formation from propenylbenzene through a carbonium ion.

Approximate thermodynamic calculations indicate that none of the stated cases are thermodynamically forbidden. The question as to which of the suggested courses is probable could be decided only by conducting counter-syntheses. The results of the counter-syntheses eliminated the first and second courses and permitted us to dwell on the third possible variant, in which the dimer is formed from propenylbenzene by structural isomerization to the styrene form, without formation of the complete α-methylstyrene molecule, with subsequent dimerization.

From literature data [7] it is known that propenylbenzene can be structurally isomerized to α-methylstyrene, and also that in the polymerization of α-methylstyrene over floridin on heating to 200° there are formed, together with polymers, two dimers: a liquid dimer (2,5-diphenylhexene-2), b.p. 302-304°, $n^{20}D$ 1.5677, d^{20}_4 0.9889, MR_D 77.11 [with composition (in %): C 91.52; H 8.48], and a crystalline dimer, m.p. 52°, to which is assigned the structure of 1,3-dimethyl-2,4-diphenylcyclobutane.

Since the dimer obtained by us and that obtained by Klages [7,8] over floridin are very similar, we considered it necessary to conduct experiments with α-methylstyrene over the aluminosilicate catalysts used in the present work.* The experiments with α-methylstyrene were carried out, over a catalyst of composition 30% Al_2O_3 and 70% SiO_2, in the liquid phase (157°, contact time 1 hour) and in the vapor phase (200°, space velocity equal to unity).

As a result of the experiments it was established that in both the liquid and the vapor phases a crystalline substance with a m.p. of 52°, a b.p. of 302-304°, and an iodine number equal to zero is formed. Obviously this substance is identical with the crystalline dimer obtained by Klages [8].

Thus, it may be considered that the hypothesis that dimerization of already-formed α-methylstyrene leads to production of 2,5-diphenylhexene-2 was not confirmed.

In order to test the second hypothesis a mixture of α-methylstyrene and propenylbenzene (1 : 1) was brought into contact with aluminosilicate.

The propenylbenzene was prepared by passing allylbenzene over aluminum oxide at a rate of 0.15-0.20 ml/min at 200°:

B.p. 174-175°, $n^{20}D$ 1.5472, d^{20}_4 0.9133. Literature data [2]: b.p. 174.5-175.5°, $n^{20}D$ 1.5475, d^{20}_4 0.9125.

On passing a mixture of α-methylstyrene and propenylbenzene over a catalyst (16% Al_2O_3 and 84% SiO_2) at 200° at a rate of 0.83 ml/cm^3-hour there was obtained a viscous, slightly fluorescent substance which did not contain an unsaturated bond:

B.p. 302-304°, $n^{20}D$ 1.5684, d^{20}_4 1.0015, MR_D 77.90.

Found %: C 91.27, 91.16; H 8.61, 8.75. M 239, 228. $C_{18}H_{20}$. Calculated %: C 91.47; H 8.53. M 236.

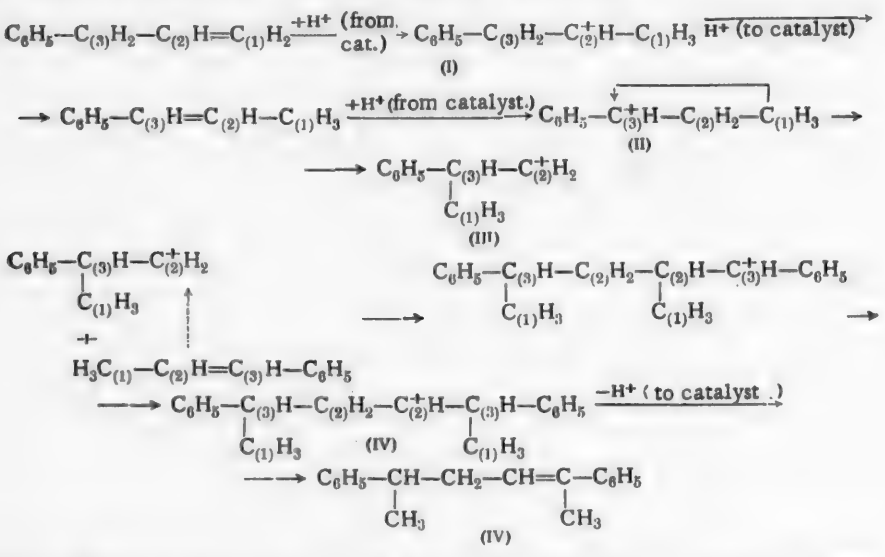
On comparison of the constants of the substance, obtained from a mixture of α-methylstyrene and propenylbenzene, with those of the substance obtained from allylbenzene, it is evident that their constants

*It must be noted that on investigation of the Raman spectra α-methylstyrene was not found in a single monomer fraction.

practically coincide. However, their infrared spectra differ substantially, which does not give grounds for considering the above-described substances identical. Consequently formation of the dimer from propenylbenzene and α-methylstyrene is also improbable.

Apparently the process of formation of 2,5-diphenylhexene-2 under our conditions goes along the third course—from propenylbenzene through its structural isomerization and formation of a carbonium ion and the subsequent reaction of the latter with a propenylbenzene molecule.

The scheme of formation of 2,5-diphenylhexene-2 is given below.



Under the influence of adsorption forces at the surface of the catalyst, excitation and shifting of the π-bond to one of the carbons of the molecule, C_1, occur. When an active hydrogen ion is present in the structure of the catalyst, and geometrical correspondence exists between the reacting molecule of the substance and the active center of the catalyst, a catalyst proton becomes attached to C_1, this being the more electronegative atom. As a result the carbonium ion (I) is formed. The carbon atom C_2 subsequently becomes attached to a pair of electrons from the adjacent atom C_3, as a result of which the bond between C_3 and the proton is weakened. Owing to this, the catalyst can now regain the proton given off earlier. As a result an electrically neutral molecule is formed, but with the double bond in a new position—propenylbenzene is obtained. Simultaneously the catalyst regains its original properties.

Further, also owing to adsorption forces at the catalyst surface, the π-bond of propenylbenzene may be excited and be shifted to C_2, which, if there is a proton in the catalyst, causes attachment of the proton to C_2. A new carbonium ion (II) is formed. In the carbonium ion thus formed, as is stated in the literature [9,10], there may occur a very simple intramolecular shift of an electron pair together with the methyl group, to which the pair is attached; in this case structural isomerization occurs, as a result of which the carbonium ion (III) is also formed.

The carbonium ion thus formed then reacts with a propenylbenzene molecule through simple addition of the olefin by means of its excess electron pair to C_2, which has a sextet of electrons. The reaction product is a carbonium ion of larger size (IV), in which intramolecular rearrangements and loss of a proton with formation of the dimer, 2,5-diphenylhexene-2, are possible.

It must be noted that with long time of contact of allylbenzene with an aluminosilicate catalyst the formation of 2,5-diphenylhexane together with 2,5-diphenylhexene-2 as a result of the redistribution of hydrogen, is possible.

SUMMARY

1. After contact of allylbenzene with aluminosilicate catalysts (at 157°) the dimer, 2,5-diphenylhexene-2, was isolated and characterized.

2. A scheme for the production of 2,5-diphenylhexene-2 over a catalyst through the formation of a carbonium ion is given.

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SYNTHESIS OF TAGGED DIETHYLAMINOETHYL S^{35}-DIPHENYL-HYDROXYTHIOACETATE

S. G. Kuznetsov, Z. I. Bobysheva and E. M. Balonova

In the study of the physiological action of cholinolytic preparations it became necessary to synthesize an active cholinolytic tagged by some radioactive atom. As the objective of synthesis, diethylaminoethyl S-diphenylhydroxythioacetate (II), which, judging from literature data [1], is a considerably more powerful acetylcholine antagonist than diethylaminoethyl S-diphenylthioacetate (thiphen), the synthesis of which with a tagged sulfur atom (S^{35}) is described in the literature [2]. At the same time, it could be expected that the synthesis of diethylaminoethyl S-diphenylhydroxythioacetate with a tagged sulfur atom would be relatively easy to accomplish, using approximately the same scheme as in the case of the synthesis of thiphen.

Diethylaminoethyl S-diphenylhydroxythioacetate was first synthesized [3] through the reaction of diphenylchloroacetyl chloride and diethylaminoethanethiol with subsequent splitting off of the chlorine in the intermediate product (I).

$$(C_6H_5)_2CClCOCl + HSCH_2CH_2N(C_2H_5)_2 \longrightarrow \underset{(I)}{(C_6H_5)_2CClCO{-}S{-}CH_2CH_2N(C_2H_5)_2} \xrightarrow{HOH} \underset{(II)}{(C_6H_5)_2C(OH)CO{-}S{-}CH_2CH_2N(C_2H_5)_2}$$

For synthesis of the aminothioester with radioactive sulfur we chose this method, modified for use with small quantities of starting materials. BaS^*O_4, containing the sulfur isotope S^{35}, was used as radioactive raw material. In a manner similar to that described for the case of tagged S^{35}-methionine [4], the BaS^*O_4 was reduced by hydrogen at 900-1000° to BaS^*, which was converted to thiourea by treatment with cyanamide and ammonium bicarbonate.

$$BaS^*O_4 \xrightarrow[900-1000^\circ]{H_2} BaS^* \xrightarrow[NH_4HCO_3]{NH_2CN} NH_2{-}CS^*{-}NH_2$$

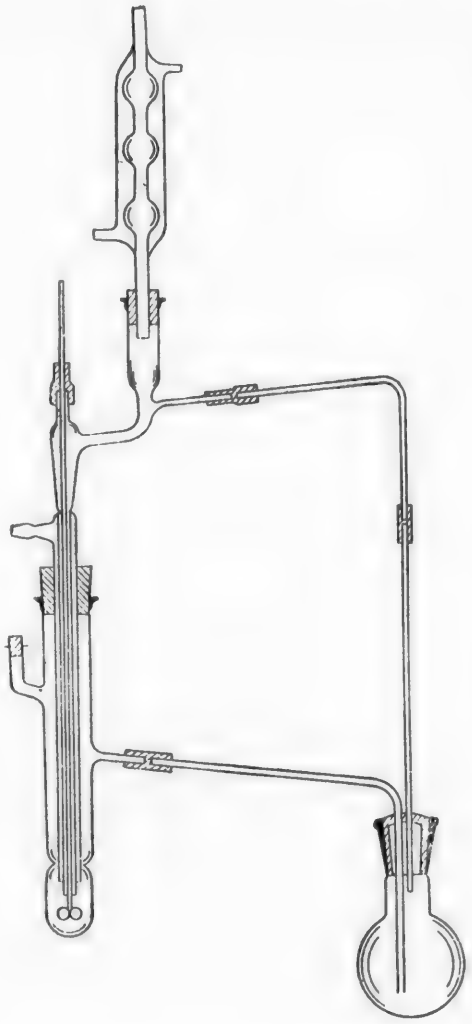
The yield of thiourea, calculated on the basis of BaS^*O_4, even in the case of small quantities of the latter (0.5-0.8 g), was about 95%. Diethylaminoethanethiol was prepared by a method based on the reaction of thiourea with diethyl-β-chloroethylamine and the alkaline hydrolysis of the β-diethylaminoethylisothiourea formed [5].

$$HCl \cdot (C_2H_5)_2NCH_2CH_2Cl + HSC(\cdot NH)NH_2 \longrightarrow$$
$$\longrightarrow HCl \cdot (C_2H_5)_2NCH_2CH_2{-}S{-}C(\cdot NH)NH_2 \cdot HCl \xrightarrow{NaOH}$$
$$\longrightarrow (C_2H_5)_2NCH_2CH_2SH + CO(NH_2)_2$$

At variance with the cited authors, both stages of the process were carried out not in alcoholic, but in aqueous solution and, furthermore, without isolation of the reaction product. To prevent oxidation of the aminomercaptan its preparation and isolation from solution were carried out in a hydrogen atmosphere in a special liquid-extractor, the construction of which is shown in the diagram.

The yield of diethylaminoethanethiol, calculated on the basis of thiourea, amounted to 70% (in work with not less than 0.7-0.8 g of thiourea). The conversion of the aminomercaptan to the final reaction product—the

aminothioester—was carried out in two stages according to the scheme given above [3]. The intermediate reaction product—diethylaminoethyl S-diphenylchlorothioacetate (I)—was isolated as the hydrochloride in the crystalline state. Diethylaminoethyl S-diphenylhydroxythioacetate (II) was initially obtained as the free base, which was then converted to the hydrochloride. The yield of aminothioester hydrochloride, calculated on the basis of diethylaminoethanethiol, amounted to 79% in work with about 5 g of the aminomercaptan and about 30% in work with 1 g of the aminomercaptan. The total yield of the final reaction product in work with small quantities (1.5-2 g) of initial $BaS{\cdot}O_4$ amounted to 20-22%, calculated on the basis of radioactive raw material. In experiments on a larger scale (8-10 g of $BaS{\cdot}O_4$), after development of the method of synthesis, the yield of diethylaminoethyl S-diphenylhydroxythioacetate hydrochloride reached 52%.



Apparatus for preparation and extraction of diethylaminoethanethiol.

It should be noted that a sample of the radioactive sulfur-containing substance prepared by the method described in the experimental part differed from an inactive sample by its noticeable reddish color, which vanished when it was dissolved in water or other solvents. In other respects both samples were identical.

EXPERIMENTAL

Barium sulfide and thiourea were prepared from $BaS{\cdot}O_4$ by methods described in the literature [2,4].

Diethylaminoethanethiol. In a liquid-extractor of 15 ml capacity (see figure), 0.83 g of thiourea and 1.87 g of diethyl-β-chloroethylamine hydrochloride were dissolved in 6.5 ml of water, and the solution was heated to boiling for 6 hours. After cooling to 60° a current of hydrogen was started, and a solution of 0.96 g of caustic soda in 2.7 ml of water was added on expulsion of the air from the system. The mixture was kept in a water bath for 1 hour at 60-70°. On cooling, enough sodium chloride was added to saturate the solution, and the aminomercaptan was extracted with ether for 4 hours. The ether extract was dried with anhydrous sodium sulfate, after which the ether was driven off in a current of hydrogen, and the aminomercaptan was distilled in vacuo from a small flask with a conical bottom. Yield, 1.0 g. B.p. 67.5° at 26 mm.

Diethylaminoethyl S-diphenylchlorothioacetate hydrochloride. To a cooled solution of 1.96 g of diphenylchloroacetyl chloride in 4 ml of dry benzene, placed in a three-neck flask, was gradually added, with stirring, a solution of 1 g of diethylaminoethanethiol in 2 ml of benzene at such a rate as to keep the temperature from exceeding 5°. The dropping funnel was washed with 0.5 ml of benzene, after which the reaction mixture was heated to 60° for 30 minutes and then cooled. The precipitated hydrochloride was filtered out, washed with ether, and dried. Yield, 2.44 g. M.p. 160-162°.

Found %: Cl 17.75, 18.02. $C_{20}H_{25}ONSCl_2$. Calculated %: Cl 17.80.

Diethylaminoethyl S-diphenylhydroxythioacetate. A solution of 2.44 g of diethylaminoethyl S-diphenylchlorothioacetate hydrochloride in 20 ml of water was kept at room temperature for 40 minutes and then at

40° for 10 minutes and was made alkaline with soda solution. The white precipitate of aminothioester base thus formed was filtered out, washed with water, and dried. After crystallization from a mixture of benzene and petroleum ether, 1.53 g of diethylaminoethyl S-diphenylhydroxythioacetate was obtained. M.p. 111-113°.

Found %: N 4.25, 4.37; S 9.42, 9.32. $C_{20}H_{25}O_2NS$. Calculated %: N 4.08; S 9.33.

Diethylaminoethyl S-diphenylhydroxythioacetate hydrochloride. The aminothioester base obtained in the preceding experiment was dissolved in the minimum quantity of absolute ethanol and neutralized with a concentrated alcoholic solution of hydrogen chloride. After addition of ether the hydrochloride crystallized out from the solution. Yield, 1.1 g. M.p. 143-146°.

Found %: Cl 9.24, 9.22. $C_{20}H_{26}NO_2SCl$. Calculated %: Cl 9.33.

SUMMARY

1. A method has been developed for the preparation of diethylaminoethyl S^{35}-diphenylhydroxythioacetate, by which the synthesis may be carried out with small amounts of BaS^*O_4 without the use of complex apparatus and in a relatively short time.

2. S^{35}-containing diethylaminoethyl S-esters of diphenylchloro- and diphenylhydroxythioacetic acids and their hydrochlorides were prepared for the first time.

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INVESTIGATIONS IN THE FIELD OF CONJUGATED SYSTEMS

LXXXIV: DIENYNE COMPOUNDS. I. SYNTHESIS AND PROPERTIES OF β-ALKOXYDIVINYLACETYLENES (ENOL ETHERS OF METHYL VINYLETHYNYL KETONE)

A. A. Petrov

β-Alkoxy derivatives of vinylacetylene were described long ago in the literature [1,2]. An attempt was made to obtain β-ethoxydivinylacetylene through the splitting off of hydrogen chloride from the addition product of ethyl hypochlorite and divinylacetylene [3]. According to analytical data, the substance obtained nearly corresponded to the expected β-ethoxydivinylacetylene; however, it was not pure (it contained 0.5% chlorine), and methylvinylethynyl ketone could not be obtained from it by hydrolysis.

We synthesized alkoxy derivatives of divinylacetylene according to the following scheme:

$$CH_2{=}CH{-}C{\equiv}CMgI + CH_2Br{-}CHBrOR \longrightarrow CH_2Br{-}CHOR{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{KOH}$$
$$\longrightarrow CH_2{=}COR{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{5\%\ H_2SO_4} CH_3{-}CO{-}C{\equiv}C{-}CH{=}CH_2$$

The corresponding bromoethers were obtained in good yields in the form of colorless oils with the odor characteristic of similar substances. They polymerize on keeping. In the presence of hydroquinone they remain unchanged for a long time. There is no doubt about their structure. It was confirmed by an investigation of the infrared spectra, in which the absorption bands of the triple (4.46 μ) and double (6.24 μ) bonds, characteristic of vinylacetylenic compounds, as well as those of the vinyl group (δ'_{ch} 10.25 and 10.77 μ), were found [4].

On treatment with alcoholic alkali the bromoethers split off hydrogen bromide even in the cold to form β-alkoxy derivatives of divinylacetylene. The latter were colorless, mobile liquids with peculiar odors. Like unsubstituted divinylacetylene [5], they show a high exaltation of the molar refraction (about 2.8).

β-Ethoxydivinylacetylene had a boiling point and refractive index near those of the substance described by A. L. Klebanskii and co-workers [3]; however, it sharply differed from the latter in its specific gravity and chemical properties—susceptibility to polymerization and hydrolysis. A. L. Klebanskii's substance begins to form a film of polymer within a few minutes after isolation, and does not give a ketone on hydrolysis. The β-ethoxydivinylacetylene isolated by us does not polymerize appreciably on keeping for a few days, and on shaking in the cold with 5% sulfuric acid it is easily hydrolyzed with formation of methyl vinylethynyl ketone, which is described in the literature. Thus the substances compared apparently have different structures.

The structures of the β-alkoxy derivatives of divinylacetylene, obtained by us, are determined with certainty by the method of synthesis, and also by hydrolysis data. In the infrared spectra of these substances the band at 4.49 μ corresponded to the triple bond, that at 6.25 μ to the double bond, and those at 10.27 and 10.76 μ to the vinyl group (δ'_{ch}).*

Methyl vinylethynyl ketone, obtained by the hydrolysis of alkoxydivinylacetylenes, has the characteristic, slightly irritating odor of acetylenic ketones. The exaltation of molar refraction, found for it, is considerably

*The infrared spectra were taken by G. I. Semenov.

higher than that for acetylenic ketones and lower than that for divinylacetylene. On keeping, it turns yellow and polymerizes. It readily forms the well-crystallized 4-nitro- and 2,4-dinitrophenylhydrazones. The latter is described in the literature [6]. Methyl vinylethynyl ketone is hydrogenated in the presence of colloidal palladium to methyl butyl ketone (identified in the form of the crystalline 2,4-dinitrophenylhydrazone).

In the infrared spectrum of the ketone a very intense band at 4.51 μ corresponds to the triple bond, one at 6.22 μ (of average intensity) to the double bond, and one at 5.94 μ to the carbonyl group. The deformation bands of the vinyl group are poorly differentiated. The high intensity and sharp decrease in frequency of the band corresponding to the triple bond in comparison with that for acetylenic ketones [7] indicate strong conjugation of the bonds in the molecule of this ketone.

EXPERIMENTAL

Preparation of bromoethers. Into a solution of ethylmagnesium iodide, prepared from 12 g of magnesium, was passed gaseous vinylacetylene (50% excess). The mixture was stirred until the evolution of ethane ceased (about 5 hours). Then, the mixture being cooled with ice, α, β-dibromodiethyl ether (100 g) or α, β-dibromoethyl butyl ether (112 g) was added. After stirring for 3 hours the reaction mixture was poured into a separatory funnel containing a mixture of ice and dilute hydrochloric acid solution. The ether layer was separated and dried over $CaCl_2$, and the ether was distilled off in a water bath. The reaction products were fractionated in vacuo. The first distillation gave a colored product; the second, a colorless one.

Thus 58 g (66% yield, based on the dibromoether) of 6-bromo-5-ethoxyhexen-1-yne-3, 7 g of a lower-boiling fraction, and 5 g of a tarry residue were obtained.

B.p. 68-69° (3 mm), 85-86° (10 mm), d^{20}_4 1.2652, $n^{20}D$ 1.5030, MR_D 47.45; calculated 46.08.

Found %: C 47.65, 47.70; H 5.61, 5.65; Br 39.24. $C_8H_{11}OBr$. Calculated %: C 47.31; H 5.46; Br 39.31.

6-Bromo-5-butoxyhexen-1-yne-3 was obtained in 85% yield.

B.p. 90-91° (3 mm), 111-112° (10 mm), d^{20}_4 1.1784, $n^{20}D$ 1.4870, MR_D 56.44; calculated 55.32.

Found %: C 51.75, 51.79; H 6.85, 7.02; Br 33.65. $C_{10}H_{15}OBr$. Calculated %: C 51.94; H 6.54; Br 34.40.

Preparation of β-alkoxydivinylacetylenes. To a 15% solution of KOH (twofold excess) in methyl alcohol, the bromoether was added through a reflux condenser. A precipitate of potassium bromide immediately formed. The liquid was boiled for 1 hour in a water bath and then was steam distilled. The alkoxydivinylacetylenes were isolated from the distillates by dilution with a saturated $CaCl_2$ solution.

β-Ethoxydivinylacetylene (2-ethoxyhexadien-1,5-yne-3) was obtained in 70% yield.

B.p. 52-52.5° (10 mm), 69-69.5° (15 mm), d^{20}_4 0.8823, $n^{20}D$ 1.5010, MR_D 40.79; calculated 37.85.

Found %: C 78.26, 78.33; H 8.40, 8.45. $C_8H_{10}O$. Calculated %: C 78.65; H 8.25.

β-Butoxydivinylacetylene (2-butoxyhexadien-1,5-yne-3) was obtained in 60% yield.

B.p. 63-64° (3 mm), 81-82° (10 mm), d^{20}_4 0.8764, $n^{20}D$ 1.4928, MR_D 49.79; calculated 47.09.

Found %: C 79.82, 79.71; H 9.59, 9.54. $C_{10}H_{14}O$. Calculated %: C 79.95; H 9.40.

Preparation of methyl vinylethynyl ketone. Five g of ethoxydivinylacetylene was agitated for 12 hours with a 5% solution of H_2SO_4 at room temperature. The mixture obtained was saturated with ammonium sulfate and the upper layer was separated, dried with $CaCl_2$, and distilled in vacuo. One and one-half g (40%) of methyl vinylethynyl ketone (hexen-1-yn-3-one-5) was obtained [6].

B.p. 38-39° (10 mm), 62.5-63° (40 mm), d^{20}_4 0.9264, $n^{15}D$ 1.4890, $n^{20}D$ 1.4842, MR_D 29.07; calculated 27.45.

Hydrazine derivatives were prepared in acetic acid solution; the 4-nitrophenylhydrazone was obtained as microscopic, short, yellow needles, m.p. 120° (from dilute alcohol).

Found %: Found %: N 18.18, 18.07. $C_{12}H_{11}O_2N_3$. Calculated %: N 18.33.

The 2,4-dinitrophenylhydrazone was obtained as orange rods, m.p. 164° (from a mixture of ethyl acetate and ethyl alcohol).

Found %: N 20.65, 20.65. $C_{12}H_{10}O_4N_4$. Calculated %: N 20.43.

For hydrogenation 0.06 g of the ketone and 1 g of palladium on $CaCO_3$ in 15 ml of methyl alcohol were taken. After absorption of 50 ml of H_2 (765 mm, 18°) the hydrogenation was stopped. To a sample of the solution was added a solution of 2,4-dinitrophenylhydrazine in acetic acid. On dilution of the liquid with water, crystals of methyl butyl ketone 2,4-dinitrophenylhydrazone, m.p. 106-107° (from dilute alcohol), precipitated [8].

Found %: N 20.47. $C_{12}H_{16}O_4N_4$. Calculated %: N 19.99.

SUMMARY

1. The ethyl and butyl ethers of divinylacetylene bromohydrin have been prepared from vinylacetylene and the corresponding α, β-dibromoethers.

2. The dehydrohalogenation products of the above ethers—β-ethoxy- and β-butoxydivinylacetylenes—are described.

3. Hexen-1-yn-3-one-5 has been prepared by the hydrolysis of β-ethoxydivinylacetylene.

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***In Russian.

INVESTIGATION OF ETHERS WITH A DOUBLE BOND IN THE ALLYL POSITION

II. SYNTHESIS OF ETHERS OF α,α,γ,γ-TETRAALKYL-SUBSTITUTED ALLYL ALCOHOLS

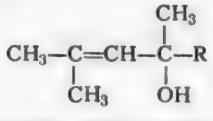
V. I. Pansevich-Kolïada and I. F. Osipenko

Aryl-substituted tertiary alcohols very readily form ethers in the presence of a number of acids, acid salts, and hydrolyzed salts [1]. It is still easier to etherify aryl-substituted alcohols containing a double bond in the allyl position by this method [2-5].

It was shown earlier by one of us [6] that 2,4-dimethylhexen-2-ol-4 (II) is also very easily etherified by methyl, ethyl, and allyl alcohols in the presence of a small quantity of dilute sulfuric acid at room temperature.

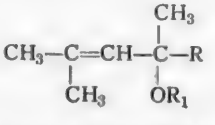
In connection with the fact that the etherification of tetraalkyl-substituted allyl alcohols has not yet been studied, and also that we found no information in the literature on the ethers obtained thereby, we investigated both the etherification of α,α,γ,γ-tetraalkyl-substituted allyl alcohols and the properties of the ethers, formed thereby, in more detail.

In the present work we carried out the etherification of 2,4-dimethylpenten-2-ol-4 (I), 2,4-dimethylhexen-2-ol-4 (II), 2,4-dimethylhepten-2-ol-4 (III), and 2,4-dimethylocten-2-ol-4 (IV) by primary monatomic alcohols of the aliphatic series.



(I) R = CH_3; (II) R = C_2H_5; (III) R = n-C_3H_7; (IV) R = n-C_4H_9

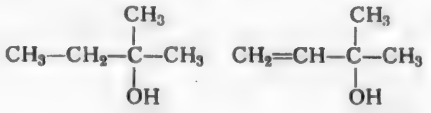
Ethers of the following structure were obtained thereby:



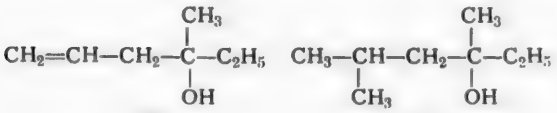
(V) R = C_2H_5, R_1 = n-C_3H_7; (VI) R = C_2H_5, R_1 = n-C_4H_9; (VII) R = C_2H_5, R_1 = iso-C_5H_{11}; (VIII) R = C_2H_5, R_1 = n-C_8H_{17}; (IX) R = n-C_3H_7, R_1 = CH_3; (X) R = n-C_3H_7, R_1 = C_2H_5; (XI) R = n-C_3H_7, R_1 = n-C_3H_7; (XII) R = n-C_3H_7, R_1 = n-C_4H_9; (XIII) R = n-C_4H_9, R_1 = CH_3; (XIV) R = n-C_4H_9, R_1 = C_2H_5; (XV) R = n-C_4H_9, R_1 = n-C_3H_7; (XVI) R = n-C_4H_9, R_1 = n-C_4H_9.

The formation of all the listed ethers takes place extremely readily. On mixing α,α,γ,γ-tetraalkyl-substituted allyl alcohols with primary monatomic alcohols containing a small quantity of dilute sulfuric acid an exothermic reaction takes place, which leads to the formation of the corresponding ether. The reaction is accompanied by a momentary turbidity of the reaction mixture, due to the water which separates out on etherification, and a 1-10° increase in temperature. The yields of ethers formed on etherification by methyl alcohol are usually the highest; the yields usually decrease on transition to higher monatomic alcohols. The structure of the monatomic alcohols has no practical effect on ether formation.

In order to elucidate the effect of the structure of tertiary alcohols on their etherification we conducted experiments on the etherification of 2-methylbutanol-2, (XVII), 2-methylbuten-3-ol-2 (XVIII), 3-methylhexen--5-ol-3 (XIX), and 2,4-dimethylhexanol-4 (XX).



(XVII) (XVIII)



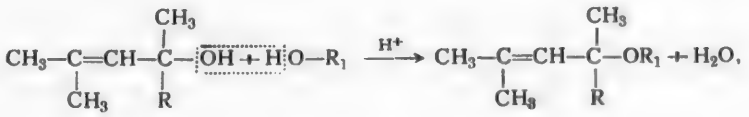
(XIX) (XX)

These alcohols are tertiary, like the $\alpha,\alpha,\gamma,\gamma$-tetraalkyl-substituted allyl alcohols (I-IV) studied by us. However, in contrast to alcohols (I-IV), alcohols (XVII) and (XX) are saturated, alcohol (XVIII) has no substituents in the γ-position, and alcohol (XIX) has a double bond in the γ,δ-position.

Our attempts to prepare the ethers of alcohols (XVII-XX) with methyl and ethyl alcohols, both under the conditions of etherification of alcohols (I-IV) and on heating at 40-60° for 5-8 hours in the presence of a small quantity of concentrated sulfuric acid, were not successful.

The unusual ease with which the etherification of alcohols (I-IV) takes place is undoubtedly due to the peculiarity of their structure. Tertiary alcohols form ethers more readily than secondary or primary, apparently because the accumulation of radicals on the carbinol carbon atom leads to weakening of the C—O bond. When a vinyl radical gem-substituted by methyl groups is present as a substituent attached to the carbinol carbon atom, this weakening is so great that easy replacement of the hydroxyl group of the tertiary alcohol by alkoxyl is possible.

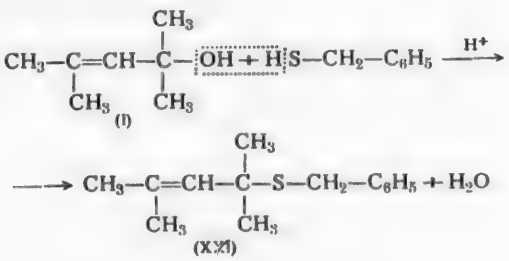
On the basis of the structural peculiarities of $\alpha,\alpha,\gamma,\gamma$-tetraalkyl-substituted allyl alcohols, their etherification by primary monatomic alcohols in the presence of acid would be expected to take place according to the scheme



i.e., as a result of cleavage of the C—O bond of the tertiary alcohol.

This scheme is in conformity with the dehydration of alcohols of this type, which takes place very readily [7], and with the easy displacement of their hydroxyl by halogen on treatment with hydrogen halide [3].

The reaction of 2,4-dimethylpentene-2-ol-4 with benzylmercaptan, which we carried out, is an indirect confirmation of the stated scheme. Under the conditions of etherification of alcohols (I-IV) these substances form the corresponding thioether—2,4-dimethyl-4-benzylthiopentene-2 (XXI) [2,4-dimethylpenten-2-yl-4 benzyl sulfide]—with the same facility. The formation of this thioether is possible only in case of cleavage of the C—O bond of the tertiary alcohol.



(I) (XXI)

The etherification of the alcohols studied by us apparently takes place through formation of an intermediate carbonium ion, the tendency toward which grows with increase in the number of substituents on the carbinol atom [8]. The mechanism of this reaction is apparently similar to that suggested for the hydrolysis of compounds containing the O–C (tert.) bond [9].

EXPERIMENTAL

Tertiary alcohols (I-IV) were synthesized by the Grignard reaction from the corresponding alkyl halides and ketones (Table 1).

TABLE 1

Characteristics of Alcohols

Name of alcohol	RX	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Literature
2,4-dimethylpenten-2-ol-4 (I)	CH_3Cl	58—60° (40)	1.4404	0.8399	35.83	35.58	[10]
2,4-Dimethylhexen-2-ol-4 (II)	C_2H_5Br	44—46 (6—7)	1.4464	0.8515	40.18	40.20	[11]
2,4-Dimethylhepten-2-ol-4 (III)	n-C_3H_7Br	61—62 (7)	1.4480	0.8508	44.74	44.82	[11]
2,4-Dimethylocten-2-ol-4 (IV)	n-C_4H_9Br	74—76 (3)	1.4505	0.8454	49.56	49.44	[11]
2-Methylbutanol-2 (XVII)	C_2H_5I	101 (737)	1.4058	0.8103	26.30	26.81	[12]
2-Methylbuten-3-ol-2 (XVIII)*		96—97 (738)	1.4175	0.8264	26.38	26.35	[13]
3-Methylhexen-5 ol-4 (XIX)	CH_2=CH—CH_2Br	48.8 (22)	1.4370	0.8250	35.42	35.58	[14]
2,5-Dimethylhexanol-4 (XX)	$(CH_3)_2$CH—CH_2Br	44.5 (10)	1.4288	0.8288	40.50	40.67	[15]

Preparation of ethers of α,α,γ,γ-tetraalkyl-substituted allyl alcohols. All the ethers were prepared by the following method. Into a three-neck flask, provided with a mechanical stirrer and seal and a thermometer, was put the tertiary alcohol. Twice the stoichiometric quantity of the primary alcohol, containing 5-10% (of the weight of tertiary alcohol taken into the reaction) of aqueous sulfuric acid solution (1 : 5), was poured into one neck with stirring. Soon the reaction mixture became turbid and slightly warmer (1-10°). Stirring was continued for 2-3 hours. After cessation of stirring, the water which had separated out in the course of the reaction was drawn off, and the reaction mixture was diluted with ether, dried with potash,** and distilled in vacuo. The ethers obtained are colorless liquids having pleasant, ethereal odors. All of them are readily soluble in organic solvents and insoluble in water, and quickly decolorize a 1% potassium permanganate solution. They do not contain active hydrogen.

The physical constants of the ethers, obtained by us, and their analyses are given in Table 2.

Ethers of 2,4-dimethylhexen-2-ol-4 (II)

2,4-Dimethyl-4-propoxyhexene-2 (V). To 10 g (0.078 mole) of alcohol (II) was added 16 g (0.214 mole) of propyl alcohol, containing 1 ml of dilute sulfuric acid. There was obtained 5.57 g (41.9%) of the ether.

2,4-Dimethyl-4-butoxyhexene-2 (VI). To 12.5 g (0.0975 mole) of alcohol (II) was added 22.5 g (0.273 mole) of butyl alcohol, containing 1 ml of sulfuric acid. There was obtained 8.22 g of the ether.

2,4-Dimethyl-4-isoamoxyhexene-2 (VII). Ten g (0.078 mole) of alcohol (II), 12.2 g (0.138 mole) of 2-methylbutanol-4, and 0.5 ml of sulfuric acid were taken. There was obtained 8.5 g of a colorless, oily liquid with an odor somewhat reminiscent of the odor of amyl alcohol.

*Alcohol (XVIII) was kindly given to us by A. A. Akhrem, for which we express to him our sincere gratitude.
**On etherification with methyl and ethyl alcohols the reaction mixture separated into layers. In this case the upper layer was drawn off, and the lower was diluted with water and extracted with ether.

TABLE 2

Characteristics of ethers of α,α,γ,γ-tetraalkyl-substituted allyl alcohols

No.	Name of ether	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Found (%)		Calc. (%)		M	
					found	calculated	C	H	C	H	found	calculated
1	2,4-Dimethyl-4-propoxyhexene-2 (V) $C_{11}H_{22}O$	57—57.9° (7)	1.4328	0.8184	54.19	54.17	77.79	13.18	77.58	13.02	170.3	170.3
2	2,4-Dimethyl-4-butoxyhexene-2 (VI) $C_{12}H_{24}O$	74—74.5 (7)	1.4355	0.8199	58.85	58.79	78.49	13.20	78.19	13.12	182.8	184.4
3	2,4-Dimethyl-4-isoamoxyhexene-2 (VII) $C_{13}H_{26}O$	79.5—80.3 (7)	1.4353	0.8169	63.41	63.41	78.89	13.45	78.72	13.21	198.2	198.3
4	2,4-Dimethyl-4-hexoxyhexene-2 (VIII) $C_{14}H_{28}O$	88—89.5 (7)	1.4401	0.8225	68.06	68.03	78.84	13.44	79.18	13.29	204.8	212.3
5	2,4-Dimethyl-4-methoxyheptene-2 (IX) $C_{10}H_{20}O$	56—56.8 (10)	1.4340	0.8197	49.63	49.55	76.85	13.12	76.86	12.90	149.9	156.2
6	2,4-Dimethyl-4-ethoxyheptene-2 (X) $C_{11}H_{22}O$	61.5—62.5 (10)	1.4344	0.8185	54.24	54.17	77.21	13.02	77.58	13.02	161.2	170.3
7	2,4-Dimethyl-4-propoxyheptene-2 (XI) $C_{12}H_{24}O$	71.5—73 (10)	1.4358	0.8179	58.92	58.79	78.45	13.24	78.19	13.12	184.4	184.4
8	2,4-Dimethyl-4-butoxyheptene-2 (XII) $C_{13}H_{26}O$	85—85.8 (8)	1.4371	0.8185	63.51	63.41	78.50	13.31	78.72	13.21	—	—
9	2,4-Dimethyl-4-methoxyoctene-2 (XIII) $C_{11}H_{22}O$	70.5—71.5 (10)	1.4375	0.8237	54.22	54.17	77.36	13.04	77.58	13.02	164.5	170.3
10	2,4-Dimethyl-4-ethoxyoctene-2 (XIV) $C_{12}H_{24}O$	76.2—76.7 (10)	1.4379	0.8214	58.90	58.79	78.44	13.15	78.19	13.12	180.1	184.4
11	2,4-Dimethyl-4-propoxyoctene-2 (XV) $C_{13}H_{26}O$	89.2—90.2 (10)	1.4389	0.8267	63.20	63.41	78.71	13.04	78.72	13.21	193.1	198.3
12	2,4-Dimethyl-4-butoxyoctene -2 (XVI) $C_{14}H_{28}O$	105—106 (10)	1.4399	0.8222	68.06	68.03	79.14	13.35	79.18	13.29	212.4	212.3

2,4-Dimethyl-4-hexoxyhexene-2 (VIII). Ten g (0.078 mole) of alcohol (II), 16.4 g (0.160 mole) of hexanol-1, and 1 ml of sulfuric acid were taken. There was obtained 8.7 g of the ether in the form of a colorless, immobile liquid.

Ethers of 2,4-dimethylhepten-2-ol-4 (III)

2,4-Dimethyl-4-methoxyheptene-2 (IX). Fifteen g (0.105 mole) of the alcohol, containing 1 ml of sulfuric acid, was taken. There was obtained 12.35 g (78%) of the ether. A colorless, mobile liquid with an agreeable odor.

2,4-Dimethyl-4-ethoxyheptene-2 (X). Fifteen g (0.105 mole) of alcohol (III), 11.82 g (0.257 mole) of ethyl alcohol, and 1 ml of sulfuric acid were taken. There was obtained 10.75 g (59.7%) of the ether.

2,4-Dimethyl-4-propoxyheptene-2 (XI). To 15 g (0.105 mole) of alcohol (III) was added 15 g (0.25 mole) of propyl alcohol, containing 1 ml of sulfuric acid. There was obtained 12.28 g (63.1%) of the ether.

2,4-Dimethyl-4-butoxyheptene-2 (XII). Fifteen g (0.105 mole) of alcohol (III) and 0.213 mole of butyl alcohol, containing 1 ml of sulfuric acid, were taken. There was obtained 10.78 g (51.3%) of the ether.

Ethers of 2,4-dimethylocten-2-ol-4 (IV)

2,4-Dimethyl-4-methoxyoctene-2 (XIII). Fifteen and sixty-two hundredths g (0.1 mole) of alcohol (IV) was etherified with 9.6 g (0.3 mole) of methyl alcohol in the presence of 0.25 ml of sulfuric acid. There was obtained 11.5 g (67.8%) of the ether. A clear, colorless liquid with an agreeable, ethereal odor.

2,4-Dimethyl-4-ethoxyoctene-2 (XIV). To 15.62 g (0.1 mole) of alcohol (IV) was added 13.8 g (0.3 mole) of ethyl alcohol, containing 1.25 ml of sulfuric acid. There was obtained 10.61 g (57.6%) of the ether.

2,4-Dimethyl-4-propoxyoctene-2 (XV). Fifteen and sixty-two hundredths g (0.1 mole) of alcohol (IV), 12 g (0.2 mole) of propyl alcohol, and 0.5 ml of sulfuric acid were taken. There was obtained 9.58 g (48.1%) of the ether.

2,4-Dimethyl-4-butoxyoctene-2 (XVI). Fifteen and sixty-two hundredths g (0.1 mole) of alcohol (IV) was etherified with 14.8 g (0.2 mole) of butyl alcohol in the presence of 1 ml of sulfuric acid. There was obtained 8.64 g (40.7%) of the ether.

Reaction of 2,4-dimethylpenten-2-ol-4 (I) with benzyl mercaptan. Twelve g (0.105 mole) of alcohol (I) was etherified with 6.5 g (0.052 mole) of benzyl mercaptan in the presence of 0.3 ml of sulfuric acid solution. The reaction mixture, which was originally a clear, homogeneous liquid, began to turn opalescent within one-half hour and then grew turbid. After standing for 2 hours, water settled on the walls and bottom of the flask in the form of drops. The odor of benzyl mercaptan was not observed. The water was separated out, and the reaction products were extracted with ether and dried with potash. As a result of distilling twice in vacuo, 4.5 g (42.4%) of 2,4-dimethyl-4-benzylthiopentene-2 was obtained; a colorless liquid with an unpleasant odor which induces headaches and nausea.

B.p. 133-134° (6 mm), $n^{20}D$ 1.5441, d^{20}_4 0.9735, MR_D 71.46; calculated 70.79.*

Found %: S 14.35, 14.70. $C_{14}H_{20}S$. Calculated %: S 14.55.

SUMMARY

1. 2,4-Dimethylhexen-2-ol-4, 2,4-dimethylhepten-2-ol-4, and 2,4-dimethylocten-2-ol-4 have been etherified by monatomic primary alcohols of the aliphatic series, and 2,4-dimethylpenten-2-ol-4 has been "etherified" by benzyl mercaptan.

2. It has been established that the presence of a vinyl radical, gem-substituted by methyl groups, on the carbinol carbon makes possible the very easy formation of ethers.

3. The formation of ethers of tetraalkyl-substituted allyl alcohols takes place apparently through displacement of the tertiary-alcohol hydroxyl by an alkoxyl group.

*The atomic refraction of thioether sulfur was taken to be 8.00 [16].

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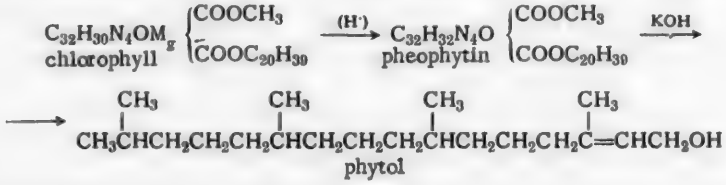
NEW SYNTHESIS OF 2,6,10,14-TETRAMETHYLHEXADECEN--15-OL-14, ISOPHYTOL

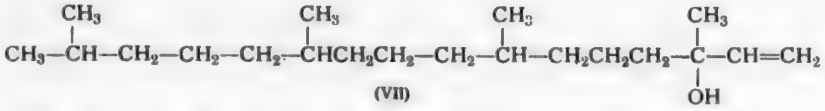
I. K. Sarycheva, G. A. Vorob'eva, N. A. Kuznetsova and N. A. Preobrazhenskii

Present-day published methods of synthesis of tocopherols (vitamins E) and α-phylloquinone (vitamin K_1) are based on the use of 2,6,10,14-tetramethylhexadecen-14-ol-16, phytol, the only source for the derivation of which is vegetable chlorophyll; 1 kg of phytol is obtained from 1 ton of technical chlorophyll [1].

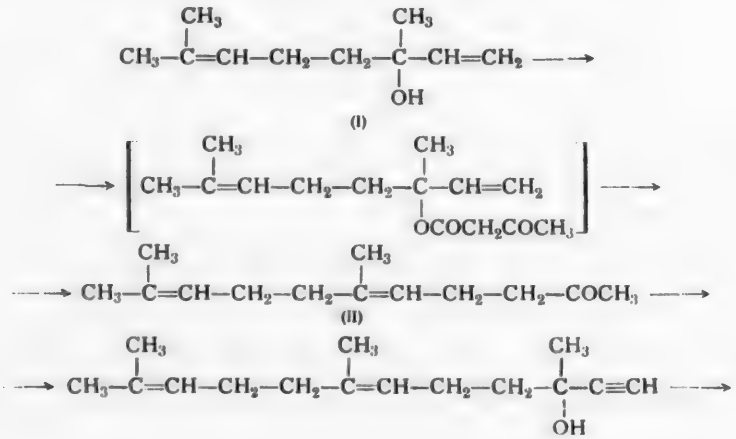


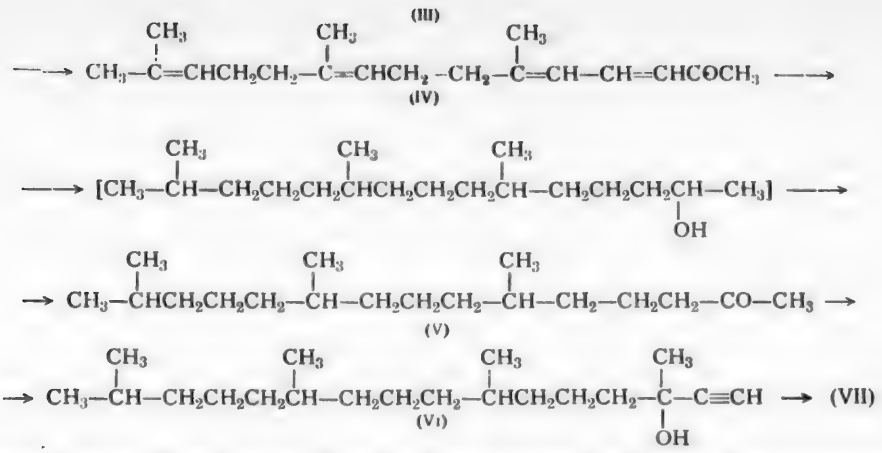
The known semisyntheses of phytol [2] are based on the use of natural terpene and sesquiterpene alcohols of the aliphatic series; hitherto they have not been widely used, either.

By investigations of the synthesis of tocopherols, α-phylloquinone, and other natural substances it has been established that the compound 2,6,10,14-tetramethylhexadecen-15-ol-14, isophytol (VII), isomeric to phytol, is fully interchangeable with phytol [3].



In the present work a new full synthesis of isophytol (VII) has been achieved.





The starting material in the synthesis is 2,6-dimethylundecadien-2,6-one-10, geranylacetone (II), which is prepared, starting from synthetic linalool [4] (I), either by means of diketene through the corresponding acetoacetate [5] (Experiment I) or by using acetoacetic ester (Experiment II) and carrying out the reaction without isolation of 2,6-dimethyloctadien-2,7-yl-6 acetoacetate. 2,6-Dimethylundecadien-2,6-one-10 (II) is converted by the action of sodium acetylide dissolved in liquid ammonia to 2,6,10-trimethyldodecadien-2,6-yn-11-ol-10, dehydronerolidol (III), which is then caused to react with acetoacetic ester. In the given case, in contrast to known syntheses of phytol and isophytol (VII) [2], the necessary lengthening of the carbon chain to C_{18} is achieved in one stage. The 2,6,10-trimethylpentadecatetraen-2,6,10,12-one-14 (IV) so synthesized is hydrogenated in the presence of Raney nickel catalyst to 2,6,10-trimethylpentadecanol-14. The latter (omitting the steps of isolation and purification) is oxidized by a mixture of potassium bichromate and sulfuric acid [chrome mixture] in acetic acid solution to 2,6,10-trimethylpentadecanone-14 (V). The latter is further condensed with sodium acetylide; the 2,6,10,14-tetramethylhexadecyn-15-ol-14 (VI) thus obtained is selectively hydrogenated in the presence of Lindlar [6] catalyst to isophytol (VII).

EXPERIMENTAL

1. 2,6-Dimethylundecadien-2,6-one-10, geranylacetone (II)

Experiment I. a) 2,6-Dimethyloctadien-2,7-yl-6 acetoacetate. To 25 g (0.162 mole) of freshly distilled linalool (I) (b.p. 80-80.5° at 10 mm) at 60° in a current of nitrogen was added 0.05 g (0.002 mole) of sodium, and the mixture was kept at 50-55° for 20 minutes. The reaction mixture was then cooled to -5°, and 15.4 g (0.183 mole) of diketene (b.p. 60-61° at 70 mm) was trickled into it in the course of 30 minutes. After standing 24 hours at 0° the mobile, yellow mass that had formed was treated with 15 ml of saturated aqueous sodium carbonate solution and extracted with 300 ml of ether. The extract was dried with sodium sulfate. After the solvent was driven off, the residue was distilled in vacuo. Yield, 31.85 g (82.4%).

B.p. 100-100.5° (1 mm), d^{20}_4 0.9761, $n^{20}D$ 1.4661, MR_D 67.63; calculated 67.58.

Found %: C 70.81, 70.55; H 8.99, 9.24. $C_{14}H_{22}O_3$. Calculated %: C 70.53; H 9.31.

b) 2,6-Dimethylundecadien-2,6-one-10, geranylacetone (II). Ten and four-tenths g of 2,6-dimethyloctadien-2,7-yl-6 acetoacetate was heated in a current of nitrogen at 155-160° for 6 hours and then distilled. Yield, 5.75 g (67.8%).

B.p. 83-84° (0.7 mm), d^{20}_4 0.8806, $n^{20}D$ 1.4690, MR_D 61.45; calculated 61.31.

Found %: C 80.17, 80.19; H 11.16, 11.24. $C_{15}H_{22}O$. Calculated %: C 80.34; H 11.41.

Experiment II. A mixture of 30 g (0.194 mole) of 2,6-dimethyloctadien-2,7-ol-6 (I) and 88 g (0.68 mole) of acetoacetic ester was heated in a current of nitrogen at 160-170° (about 50 hours). The unreacted acetoacetic ester was then driven off from the reaction mass. The residue was distilled. Yield, 21 g (55.6%).

B.p. 118-120° (7 mm), d^{20}_4 0.8801, $n^{20}D$ 1.4689, MR_D 61.44. $C_{15}H_{22}O$. Calculated 61.31.

2. 2,6,10-Trimethyldodecadien-2,6-yn-11-ol-10, dehydronerolidol (III)

Into 750 ml of liquid anhydrous ammonia was passed a rapid current of dry acetylene, and 23 g (1 mole) of sodium was simultaneously added, with stirring, at such a rate as to avoid the production of a persistent blue color in the reaction mass. The flow rate of the acetylene was decreased, and 100 g (0.52 mole) of 2,6-dimethylundecadien-2,6-one-10 (II) was then added in the course of 40 minutes, after which the mixture was stirred for 2 hours and allowed to stand for 16 hours at room temperature. The thick, yellow mass thus formed was treated at -5° with 600 ml of ice water and acidified with sulfuric acid (d^{20}_4 1.395) to a pH of 6.5. Separation of layers occurred; the oily upper layer was drawn off, and the lower one was extracted with 500 ml of ether. The combined extracts were dried with sodium sulfate. After solvent removal the residue was distilled. Yield, 80.5 g (70.9%).

B.p. 107-110° (2.5 mm), d^{20}_4 0.8894, $n^{20}D$ 1.4790, MR_D 70.23; calculated 70.06.

Found %: C 81.87, 81.74; H 10.69, 10.83. $C_{15}H_{24}O$ Calculated %: C 81.80; H 10.98.

3. 2,6,10-Trimethylpentadecatetraen-2,6,10,12-one-14 (IV)

A mixture of 70 g (0.317 mole) of 2,6,10-trimethyldodecadien-2,6-yn-11-ol-10 (III) and 155 g (1.192 moles) of freshly distilled acetoacetic ester was heated in a current of nitrogen at 165–170° for 55 hours; evolution of carbon dioxide was observed. The unreacted acetoacetic ester was driven off from the reaction mass. The residue was distilled. Yield, 44.93 g (54.3%).

B.p. 110-111° (0.3 mm), 125-127° (0.6 mm), d^{20}_4 0.9114, $n^{20}D$ 1.4951, MR_D 82.85; calculated 83.47.

Found %: C 82.66, 82.79; H 10.65, 10.95. $C_{18}H_{28}O$. Calculated %: C 83.09; H 11.09.

4. 2,6,10-Trimethylpentadecanone-14 (V)

Ninety g of 2,6,10-trimethylpentadecatetraen-2,6,10,12-one-14 (IV) was hydrogenated for 2 hours at 95-100° in a rotary autoclave in the presence of 10 g of Raney nickel catalyst and 100 ml of ethyl alcohol. Initial hydrogen pressure, 90 atm. After cooling to room temperature (45 atm. pressure) the autoclave was emptied, and the catalyst was filtered off and washed with 100 ml of ethyl alcohol. The solvent was distilled off from the combined filtrates. The residue, which amounted to 89 g, had the form of a viscous, light-orange oil. To a mixture of 50 g of the latter and 22.5 g of potassium bichromate in 150 ml of water and 61 g of glacial acetic acid was added 29 ml of sulfuric acid (d^{20}_4 1.395) with stirring in a current of nitrogen. The temperature of the reaction mass thereupon increased spontaneously to 60°. In order to complete the reaction the mixture was heated for 50 minutes at 80-85°. After cooling to room temperature 50 ml of ether was added to it. The upper layer was drawn off, and the lower one was extracted with 200 ml of ether. The ether extract was washed with a saturated aqueous solution of sodium carbonate and dried with sodium sulfate. After the solvent was driven off, the residue was distilled in vacuo. Yield, 34.4 g (69.29%, calculated on the basis of 2,3,6-trimethylpentadecatetraen-2,6,10,12-one-14).

B.p. 110-113° (0.2 mm), d^{20}_4 0.8740, $n^{20}D$ 1.4652, MR_D 84.94; calculated 85.33.

Found %: C 80.21, 80.78; H 13.25, 13.00. $C_{18}H_{36}O$. Calculated %: C 80.52; H 13.52.

5. 2,6,10,14-Tetramethylhexadecyn-15-ol-14 (VI)

To sodium acetylide prepared from 1.83 g (0.08 mole) of sodium and dry acetylene in 100 ml of anhydrous liquid ammonia was added a solution of 10 g (0.037 mole) of 2,6,10-trimethylpentadecanone-14 (V) in 12 ml of anhydrous ether during 15 minutes. The reaction mixture was stirred for 1 hour and allowed to stand for 15 hours at room temperature. The thick, dark-yellow mass thus formed was treated with 30 ml of ice water and was acidified with 15 ml of sulfuric acid (d^{20}_4 1.395) to a pH of 6.5. Separation into layers occurred; the upper layer was drawn off, and the lower one was extracted with 50 ml of ether. The combined extracts were dried with sodium sulfate. After solvent removal the residue was distilled. Yield, 5.9 g (53.6%).

B.p. 119-121° (0.2 mm), d^{20}_4 0.8798, $n^{20}D$ 1.4698, MR_D 93.35; calculated 94.08.

Found %: C 81.30, 81.12; H 12.93, 12.81. $C_{20}H_{38}O$. Calculated %: C 81.56; H 13.00.

6. 2,6,10,14-Tetramethylhexadecen-15-ol-14, isophytol (VII)

Four g of 2,6,10,14-tetramethylhexadecyn-15-ol-14 (VI) in 40 ml of petroleum ether (b.p. 80-105°) was hydrogenated at 20° in the presence of 0.6 g of palladium catalyst and 0.16 g of quinoline with mechanical agitation. After absorption of 320 ml of hydrogen (105% of the theoretical amount) the hydrogenation was stopped. The catalyst was filtered off and washed with 15 ml of petroleum ether. The combined filtrates were treated with sulfuric acid (d^{20}_4 1.032) and with sodium bicarbonate solution and dried with sodium sulfate. After the solvent was driven off, the residue was distilled. Yield, 3.4 g (84.41%).

B.p. 114-115° (0.4 mm), d^{20}_4 0.8680, $n^{20}D$ 1.4718, MR_D 95.21; calculated 95.61.

Found %: C 81.25, 81.17; H 13.40, 13.62. $C_{20}H_{40}O$. Calculated %: C 81.02; H 13.61.

SUMMARY

1. A full synthesis of 2,6,10,14-tetramethylhexadecen-15-ol-14, isophytol, has been achieved.

2. In the course of the synthesis 2,6,10-trimethylpentadecatetraen-2,6,10,12-one-14, 2,6,10-trimethylpentadecanone-14, and 2,6,10,14-tetramethylhexadecyn-15-ol-14 were isolated and characterized.

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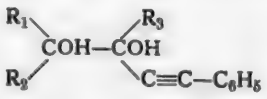
INVESTIGATION OF THE CONVERSION OF PINACOLS WITH SUBSTITUTED ACETYLENE RADICALS

XV. ACTION OF MERCURIC SULFATE ON UNSYM. DIMETHYLPHENYL (PHENYLETHYNYL)- AND UNSYM. METHYLDIPHENYL (PHENYLETHYNYL) ETHYLENE GLYCOLS

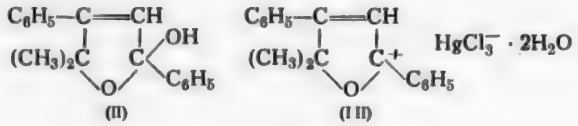
L. A. Pavlova, A. Fabritsy and E. D. Venus-Danilova

In earlier reports by one of us together with A. Fabritsy were given the results of the reactions of unsym. dimethylphenyl (phenylethynyl) ethylene glycol (2-methyl-3,5-diphenylpentyn-4-diol-2,3) (Ia) and unsym. methyldiphenyl (phenylethynyl) ethylene glycol (2-methyl-1,1,4-triphenylbutyn-3-diol-1,2) (Ib) with mercuric chloride and mercuric acetate [1,2], and also that of trimethyl (phenylethynyl) ethylene glycol (2,3-dimethyl--5-phenylpentyn-4-diol-2,3) (Ic) with mercuric chloride [3].

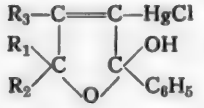


(Ia) $R_1 = R_2 = CH_3$; $R_3 = C_6H_5$.
(Ib) $R_1 = R_2 = C_6H_5$; $R_3 = CH_3$.
(Ic) $R_1 = R_2 = R_3 = CH_3$.

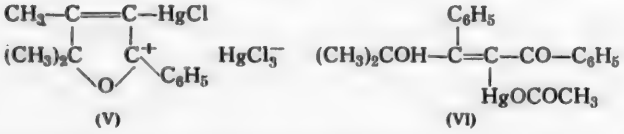
Moreover, it was found that unsym. dimethylphenyl (phenylethynyl) ethylene glycol (Ia), on reaction with mercuric chloride in alcoholic solution, forms not only the isomerization product of the glycol—5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 (II)—but also a complex mercury salt of this 2-hydroxydihydrofuran (III), and a mercuration product of the 2-hydroxydihydrofuran (IVa), which was found, on treatment with ammonia, in the form of the symmetrization product [1].



(II) (III)



(IVa) $R_1 = R_3 = CH_3$; $R_2 = C_6H_5$
(IVb) $R_1 = R_2 = R_3 = CH_3$.



(V) (VI)

On treatment of trimethyl (phenylethynyl) ethylene glycol (Ic) with mercuric chloride the analogous organomercuric compound (IVb) and a complex mercuric salt of the latter (V) are obtained.

In the reaction of mercuric acetate with unsym. dimethylphenyl (phenylethynyl) ethylene glycol (Ia) the mercuration product (VI), corresponding to the open form of the 2-hydroxydihydrofuran (II) [2], was successfully isolated.

Unsym. methyldiphenyl (phenylethynyl) ethylene glycol (Ib) in the presence of mercuric chloride behaves quite differently, forming the glycol dimer, $C_{46}H_{36}O_2$, with liberation of two molecules of water; with mercuric acetate an addition product of mercuric acetate with the glycol is apparently obtained [3].

In view of the fact that we have hitherto not succeeded in finding hydration products of acetylenic ditertiary α-glycols (Ia, b, c) when using mercury salts (mercuric chloride, bromide, and acetate), we decided to employ mercuric sulfate and to investigate the products of transformation of unsym. dimethylphenyl (phenylethynyl) ethylene glycol (Ia) and unsym. methyldiphenyl (phenylethynyl) ethylene glycol (Ib) in the presence of this mercury salt.

In this case it was found that unsym. methyldiphenyl (phenylethynyl) ethylene glycol (Ib) is converted on treatment with mercuric sulfate, both in aqueous solution in the presence of a little sulfuric acid and in acetone solution, to the dimer, $C_{46}H_{36}O_2$, described earlier by us [3].

Although the structure of the dimer obtained requires additional proof, it may be assumed that as a result of dehydration and molecular rearrangements 2,5,5-triphenyl-4-vinyldihydrofuran-4,5 is initially formed and then dimerizes like 2,3,3,4-tetramethyl-2-(β,β-dimethylvinyl) dihydrofuran-2,3 [4].

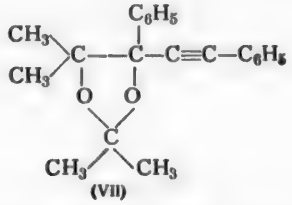
The same dimer was obtained on treatment of glycol (Ib) with mercurous sulfate.

Simultaneously glycol (Ib) was heated for 5 hours with dilute sulfuric acid without addition of mercuric sulfate. In this experiment the glycol was recovered unchanged. This was to be expected, since it is known that unsym. methyldiphenyl (phenylethynyl) ethylene glycol is very stable with respect to sulfuric acid and gives a ketone of the acetylene series only on heating with 40% sulfuric acid [5].

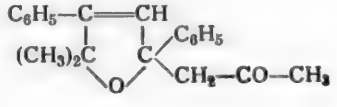
Unsym. dimethylphenyl (phenylethynyl) ethylene glycol (Ia) was treated with mercuric sulfate under various conditions: in aqueous solution, in aqueous solution in the presence of a little sulfuric acid, and in acetone solution. In the first two experiments the isomerization product of the glycol—5,5-dimethyl-2,4--diphenyl-2-hydroxydihydrofuran-2,5 (II)—was obtained. On treatment of the glycol with mercuric sulfate in acetone solution a viscous oil was formed, which gave no sign of the presence of a hydroxyl group and very slowly decolorized a solution of bromine in chloroform, and also potassium permanganate solution; it dissolved in concentrated sulfuric acid with a beautiful, blue fluorescence. The product obtained was successfully purified by distillation in vacuo with a high pumping rate.

The same substance was obtained on treatment of the glycol with mercurous sulfate in acetone solution.

According to the data of elementary analysis and molecular weight, this substance may be either an isopropylidene derivative of the glycol (VII) or a condensation product of hydroxydihydrofuran (II) with acetone—5,5-dimethyl-2,4-diphenyl-2-acetonyldihydrofuran-2,5 (VIII).



(VII)



(VIII)

It was found that the substance obtained is hydrolyzed by 10% sulfuric and 70% acetic acids with the formation of acetone and hydroxydihydrofuran (II). This fact, however, does not yet provide a basis for assigning the structure of the condensation product (VIII) to this substance, since hydroxydihydrofuran (II) may be not the initial product of hydrolysis, but a product formed by isomerization of the glycol under the influence of acid (experiments with 10% sulfuric and 70% acetic acids showed that conversion of the glycol to the hydroxydihydrofuran can take place under these conditions).

In order to solve the problem of the structure of the substance obtained on treatment of an acetone solution of the glycol with mercuric sulfate, we decided to synthesize this substance by another route. Firstly, experiments on the preparation of the isopropylidene derivative (VII) were conducted. For this the acetone solution of the glycol was saturated with hydrogen chloride and allowed to stand for several days [6]. In this case the isopropylidene derivative was not obtained. After neutralizing the solution and distilling off the acetone

the original glycol was recovered. Heating of the acetone solution of the glycol with calcined cupric sulfate was also without result.

On the other hand, we attempted to prepare substance (VIII) by condensation of hydroxydihydrofuran (II) with acetone. Heating an acetone solution of hydroxydihydrofuran (II) in a sealed tube, without catalysts and in the presence of calcined cupric sulfate, did not lead to condensation. By heating the acetone solution of hydroxydihydrofuran (II) with mercuric sulfate we obtained a substance which was identical with the product obtained under these conditions from the glycol. On the basis of this experiment the substance obtained from the glycol in acetone solution on treatment with mercuric sulfate may be regarded as 5,5-dimethyl-2,4-diphenyl-2-acetonyl-dihydrofuran-2,5.

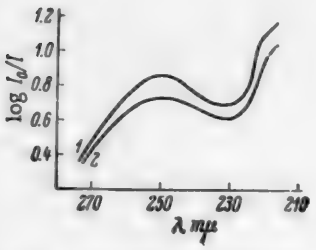


Fig. 1. Ultraviolet absorption spectrum of 5,5-dimethyl-2,4-diphenyl-2-acetonyldihydrofuran-2,5 in ethyl alcohol. 1) Substance obtained from the glycol (Ia) (0.73×10^{-4} mole) [0.7310^{-4}]; 2) substance obtained from the hydroxydihydrofuran (II) (0.69×10^{-4} mole) [0.6910^{-4}].

In order to confirm the identity of the substances obtained from unsym. dimethylphenyl (phenylethynyl) ethylene glycol (Ia) and 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 (II), their absorption spectra in the ultraviolet region• were taken (Fig. 1).

It may be assumed that under the influence of either mercurous or mercuric sulfate the glycol isomerizes to the hydroxydihydrofuran, and the latter condenses with acetone.

It was shown earlier that the hydroxyl group in 2-hydroxydihydrofurans-2,5 has high mobility. This is manifested in reduction [7], in the formation of ketal-type ethers [8], and in condensation with phenylmethylpyrazolone [9]. In this connection the hydroxydihydrofurans are similar to arylcarbinols, for which numerous condensation reactions are known, in particular the condensation of the base of crystal violet (or better, its methyl ether) with acetic and propionic aldehydes [11].

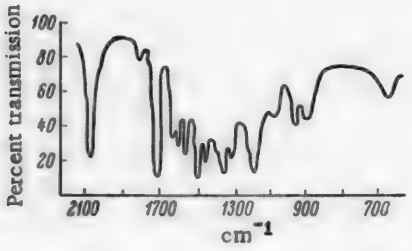


Fig. 2. Infrared spectrum of 5,5-dimethyl-2,4-diphenyl-2-acetonyldihydrofuran-2,5.

We were unable to prepare carbonyl derivatives of the isolated condensation product, but in the infrared absorption spectrum•• of the substance (Fig. 2) there is an intense band with a frequency of 1710 cm^{-1}, characteristic of the carbonyl group [12]. The deformation frequency δ'_{CH} of the $\diagdown C = CH \diagup$ group, 883 cm^{-1}, is also found in the spectrum; the characteristic frequency of the triple bond is not found.

EXPERIMENTAL

I. Action of mercuric sulfate on unsym. dimethylphenyl (phenylethynyl) ethylene glycol (Ia)

Experiment 1. Two and one-half g of the glycol, 3.5 g of $HgSO_4$, 50 ml of water, and 1.5 ml of H_2SO_4 (sp. gr. 1.83) were heated to boiling for 3 hours. The mixture, which became yellow on heating, was cooled, and the precipitate was filtered off and washed with ether and water. The precipitate weighed 3 g (according to analysis for mercury, the precipitate was the basic salt $HgSO_4 \cdot 2HgO$). From the solution an ether extract was made, which after drying and elimination of ether gave 1.85 g of a clear, rose-colored oil which soon crystallized. After purification the crystalline substance did not give a melting point reduction when mixed with hydroxydihydrofuran (II). From the neutralized aqueous solution 0.5 g more of hydroxydihydrofuran (II) was isolated. The total yield of crude product was 94%.

• The ultraviolet spectrum was taken with an SF-4 spectrograph.

•• The infrared spectrum was taken with an IKS-2 apparatus, having NaCl and LiF prisms, in a 2% solution in CCl_4 with a layer thickness of 1 mm.

Experiment II. Two and one-half g of the glycol, 3.5 g of $HgSO_4$, and 50 ml of water were heated to boiling for 3 hours. At the beginning of the experiment nearly all the material passed into solution, whereupon the entire volume became turbid. After cooling, 2 g of a precipitate was separated out (in its Hg^{++} and SO_4^{--} content the precipitate was similar to the basic salt $HgSO_4 \cdot 2HgO$). An ether-benzene extract was made from the solution, after which the latter was neutralized with soda and treated with ether. After elimination of solvent from the extract made from the acid solution, 2 g of a viscous oil, which crystallized on trituration with benzene, was obtained. The substance obtained did not give a melting point reduction when mixed with hydroxydihydrofuran (II). From the extract obtained from the neutralized solution 0.2 g of a reddish oil, which crystallized after a brief time and also consisted of hydroxydihydrofuran (II), was isolated. The total yield of crude product was 88%.

Experiment III. To a solution of 15 g of the glycol in 200 ml of acetone (dried over $CaCl_2$ and distilled) was added 15 g of $HgSO_4$, and the mixture was heated to boiling, with stirring, for 4 hours. On the following day the precipitate was filtered off and washed with acetone (14.8 g of a substance similar, according to its analysis for mercury, to mercuric sulfate was obtained). From the filtrate, combined with the wash liquids, the acetone was distilled off at a low rate. On concentration of the solution in a distilling flask a small, yellow precipitate was formed, which was subsequently filtered off. The yellow substance (0.4 g)—acicular crystals, m.p. 177-180° (decomp.)—is soluble in ether and in alcohol, is insoluble in benzene and in petroleum ether, and contains mercury. It was not further investigated.

The oil, remaining after separation of the yellow, crystalline substance, was diluted with petroleum ether, freed from precipitated sludge by filtration, washed with water, and dried with sodium sulfate. The viscous liquid obtained after distilling off the petroleum ether, carefully freed from remnants of solvent, was distilled in vacuo. A viscous, light-yellow liquid, b.p. 170-171° (0.22 mm), was obtained. A considerable tarry residue remained in the distilling flask, and a deposit of mercury was found in the side arm. Apparently, a small quantity of the yellow, crystalline product containing mercury was dissolved in the oil and decomposed on distillation in vacuo.

The fraction with a b.p. of 170-171° (0.22 mm) was redistilled. Yield, about 50%.

B.p. 160-161° (0.2 mm), d^{20}_4 1.1120, $n^{20}D$ 1.5728, MR_D 90.65; calculated (VIII) 90.96.

Found %: C 82.69, 82.79; H 6.97, 6.81. M 309. $C_{21}H_{22}O_2$. Calculated %: C 82.35; H 7.19. M 306.

Hydrolysis of the substance obtained. Four g of the product with a b.p. of 160-161° (0.2 mm) was heated with 30 ml of 10% sulfuric acid and 10 ml of alcohol in a water bath for 1.5 hours. The reaction mixture was cooled, partially neutralized with potash, and steam distilled. The distillate was collected in a receiver containing a solution of 2,4-dinitrophenylhydrazine. Immediately there formed a precipitate, m.p. 126°, which did not give a melting point depression when mixed with acetone 2,4-dinitrophenylhydrazone.

The residual mixture was completely neutralized and treated with ether. After the ether was distilled off, an oil was obtained, which partially crystallized. The crystals were separated and purified. There was obtained 2.1 g (60%) of a substance which did not give a melting point depression when mixed with the hydroxydihydrofuran (II). The remainder of the oil (1.4 g) did not crystallize, and after long standing had $n^{20}D$ 1.5740.

Experiment IV. Six g of hydroxydihydrofuran (II), 6 g of $HgSO_4$, and 60 ml of acetone were heated to boiling for 4 hours. The reaction mixture was treated as in Experiment III, whereupon no changes in comparison with Experiment III were observed. The oily product obtained was identical in properties with the substance obtained in Experiment III: it did not react with methylmagnesium iodide, it slowly decolorized a solution of bromine in chloroform, and also potassium permanganate solution, and on addition of a minute quantity of the substance to concentrated sulfuric acid a blue fluorescence appeared. On distillation in vacuo the main part of the substance passed over at 181-182° (0.4 mm); yield, 3.8 g (55%).

d^{20}_4 1.1014, $n^{20}D$ 1.5703, MR_D 91.19; calculated 90.96.

Found %: C 82.52, 82.54; H 7.54, 7.55. M 303.6. $C_{21}H_{22}O_2$. Calculated %: C 82.35; H 7.19. M 306.

The IR spectrum of the substance obtained in Experiment IV, taken in the 1590-1730 cm^{-1} region, coincides well with that of the substance obtained in Experiment III (Fig. 2).

Experiment V was conducted with a solution of 10 g of the glycol in 125 ml of acetone, to which was added 10 g of Hg_2SO_4, under the conditions of Experiment III. From the reaction products 9.6 g of a grayish precipitate of the mercury salt was obtained. The filtrate was treated as in Experiment III. On concentration of the filtrate separation of a small quantity of a yellow substance containing mercury was again observed. The oil obtained was distilled in vacuo: 1st fraction, 150-154° (0.24 mm), $n^{20}D$ 1.5711; 2nd fraction, 154-163° (0.24 mm), $n^{20}D$ 1.5721.

There was a considerable gray deposit in the side arm and a rather large tarry residue in the bulb.

The 2nd fraction was redistilled. The main mass passed over at 166-172° (0.3 mm), $n^{20}D$ 1.5730. The part of this distillate having a b.p. of 169-170° (0.3 mm), was withdrawn for analysis.

B.p. 169-170° (0.3 mm), d^{20}_4 1.1056, $n^{20}D$ 1.5721, MR_D 91.08; calculated 90.96.

Found %: C 82.65, 82.51; H 7.39, 7.36. M 304. $C_{21}H_{22}O_2$. Calculated %: C 82.35; H 7.19. M 306.

II. Action of mercuric sulfate on unsym. methyldiphenyl (phenylethynyl) ethylene glycol (Ib)

Experiment I. A mixture of 3 g of the glycol (m.p. 120-121°), 2.9 g of $HgSO_4$, and 60 ml of water, to which had been added 1.5 ml of H_2SO_4 (sp. gr. 1.83), was heated to boiling for 2 hours. Next day the reaction mixture had acquired an orange color, and a benzene extract of it gave 2 g of reddish, tarry product, which was dissolved several times in ether and precipitated with alcohol. From the alcoholic-ethereal mixture a yellowish, amorphous substance, m.p. 108-117°, which did not contain mercury, separated out.

Found %: C 88.80, 88.78; H 5.98, 6.00. M 624. $C_{46}H_{36}O_2$. Calculated %: C 89.03; H 5.83. M 620.

Experiment II. Four g of the glycol, 3.7 g of $HgSO_4$, and 65 ml of acetone were heated to boiling for 3 hours. After distilling off the acetone a dark oil was obtained, which was dissolved in ether. On addition of a large amount of alcohol to the ether solution a yellowish, amorphous powder separated out, which was identical with the product obtained in Experiment I and that obtained earlier on treatment of glycol (Ib) with mercuric chloride [3].

Experiment III. Two g of glycol (Ib), 1.9 g of Hg_2SO_4, 40 ml of water, and 1 ml of H_2SO_4 (sp. gr. 1.83) were heated to boiling for 5 hours with stirring. At first the glycol floated on the surface, while the Hg_2SO_4 lay chiefly at the bottom. Gradually an oily substance appeared, which enveloped the mercury salt, and on the stirrer a lump formed, which hardened on cooling. The hard mass was agitated with ether. Thereupon the organic part passed into solution, and the Hg_2SO_4 (1.75 g) formed a precipitate. Isolation and purification were carried out as in Experiment I. There was isolated 1.7 g (82%) of an amorphous substance, melting in the interval 107-119°, which was quite similar to the dimer obtained on treatment of glycol (Ib) with $HgSO_4$ or $HgCl_2$ [3].

Found %: C 89.27; H 5.53. M 607. $C_{46}H_{36}O_2$. Calculated %: C 89.03; H 5.89. M 620.

The same substance was also obtained on treatment of glycol (Ib) with Hg_2SO_4 in the presence of acetone.

SUMMARY

1. It has been shown that unsym. dimethylphenyl (phenylethynyl) ethylene glycol (2-methyl-3,5-diphenylpentyn-4-diol-2,3) is converted to 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 on treatment with mercuric sulfate.

2. It has been established that in the presence of mercuric sulfate 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 condenses with acetone, forming 5,5-dimethyl-2,4-diphenyl-2-acetonyldihydrofuran-2,5, which is not described in the literature.

3. Unsym. methyldiphenyl (phenylethynyl) ethylene glycol forms a dimer of uncertain structure on treatment with mercuric sulfate.

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INVESTIGATION IN THE FIELD OF VAPOR-PHASE CATALYTIC HYDRATION OF ACETYLENE AND ITS DERIVATIVES

I. HYDRATION OF VINYLACETYLENE TO METHYL VINYL KETONE

Iu. A. Gorin and L. P. Bogdanova

The addition of water to vinylacetylene in the liquid phase under the influence of mercury salts to form methyl vinyl ketone was first accomplished by J. Nieuwland [1]. This reaction was later studied by a number of authors [2-5]. I. N. Nazarov [6] carried out the hydration of vinylacetylene in alcoholic solutions, and he thus obtained methyl β-alkoxyethyl ketones in 55-90% yields, calculated on the basis of the vinylacetylene taken. Other methods of obtaining methyl vinyl ketone are also known [7-9], but the method of preparation of the latter by hydration of commercial vinylacetylene is the simplest.

The reaction between water and acetylene may also be carried out in the vapor phase under the influence of various solid catalysts. There are a number of patents, journal articles, and reviews [10] in which the use of oxides and various salts of zinc, copper, and cadmium (phosphates, tungstates, and other salts of these metals), as well as mixtures of certain of these with phosphoric acid, as catalysts for this process, is described. In many cases these catalysts are deposited on carriers, among which activated charcoal, calcium phosphate, "cuprene", and a number of other substances are mentioned. The employment of such catalysts for the process of hydration of acetylene to aldehyde makes it possible to abandon the use of mercury salts, which are toxic substances.

If the problem of vapor-phase hydration of acetylene has received a relatively great amount of attention, no one has been engaged in the study of hydration reactions of acetylene derivatives over solid catalysts, although the investigation of these processes may have not only theoretical interest, but also practical importance as one of the ways of obtaining ketones useful as starting materials for various organic syntheses.

Methyl vinyl ketone—a product of the hydration of vinylacetylene—may be used for various syntheses [11-13], including one of the steps in the synthesis of vitamin A [14,15]. In the latter case the use of methyl vinyl ketone prepared from vinylacetylene by treatment with mercury salts is undesirable, since traces of mercury may remain in the final product and may pass into the human organism. Obviously methyl vinyl ketone obtained through the vapor-phase hydration of vinylacetylene over catalysts not containing mercury must be free from the stated faults.

In the present work it is shown that solid catalysts such as zinc oxide, cadmium tungstate, cadmium-calcium-phosphate catalyst, and tungsten trioxide may be used for the successful hydration of vinylacetylene to methyl vinyl ketone in the gas phase. In carrying out the process the hydrocarbon is diluted with 10 times its volume of steam. The methyl vinyl ketone thus formed is found among the reaction products, partly in the aqueous solution and partly in the upper oil layer, from which it may be recovered by rectification. Together with methyl vinyl ketone, a small quantity of vinylacetylene polymerization products (mainly the trimer, apparently) and a dimer of methyl vinyl ketone (2-acetyl-6-methyl-2,3-dihydropyran) are obtained.

The results of the effect of the temperature and space velocity of the vinylacetylene on the process of hydration of the latter in the presence of various catalysts are given in the table. A comparative evaluation of the activity and selectivity of action of the catalysts investigated may be made by comparing the results of experiments 1, 7, 12, and 17, which were carried out under the same conditions of space velocity and dilution of the hydrocarbon with steam (1 : 10) and in which about the same degree of conversion of vinylacetylene was obtained.

TABLE

Effect of Temperature and Space Velocity on the Process of Hydration of Vinylacetylene Over Various Catalysts (Average Data of Three Experiments)

Experiment No.	Name of Catalyst	Temperature of experiment	Space vel. vinylacetylene (1/l cat./hr)	Deg. conversion methylvinylacetylene (in %)	Methyl vinyl ketone on basis of reacted vinylacetylene (in %)	Productivity with respect to methyl vinyl ketone (g/l cat./hr)
1	Cadmium tungstate	325°	100	31.8	87.0	85
2		350	100	50.5	76.0	121
3		375	100	59.0	73.2	133
4		375	150	35.0	81.0	131
5		400	150	57.5	70.0	188
6	Cadmium phosphate on calcium phosphate $\frac{CdO + CaO}{P_2O_5} = 2.88$	350	100	24.1	78.0	62
7		375	100	32.8	72.5	79
8		400	100	39.1	52.5	63
9		350	150	19.7	83.0	80
10		375	150	24.3	80.0	91
11	Tungsten trioxide	350	100	27.6	74.5	62
12		375	100	38.8	69.0	81
13		400	100	52.2	65.5	103
14		350	70	48.7	71.5	76
15	Zinc oxide	375	100	14.3	91.0	38
16		400	100	17.7	84.5	36
17		425	100	32.4	75.5	78
18		400	70	20.4	81.6	41

It follows from the data of the table that cadmium tungstate has the greatest catalytic activity and selectivity with respect to yield of methyl vinyl ketone. For equal space velocities of vinylacetylene, the same degree of conversion of the latter is attained with this catalyst at a lower temperature than with the other catalysts. Lower results were obtained with a cadmium-calcium-phosphate catalyst with a ratio of acid and basic salts, equal to 2.88. Maximum yields of methyl vinyl ketone, obtained under optimum conditions with the above-mentioned catalysts, are not inferior to results obtained, according to literature data, on hydration of vinylacetylene in the liquid phase with mercury catalysts. Investigation of the duration of one contact cycle showed that after 3 hours of use the activity of the catalysts begins to fall as a result of deposition of polymers and resins on their surfaces. The activity of the catalyst may be restored through regeneration at 400-450° in a current of air mixed with steam. The least fall of activity (degree of conversion of vinylacetylene and productivity with regard to methyl vinyl ketone) is observed for a cadmium-calcium-phosphate catalyst in which the ratio $\frac{CdO + CaO}{P_2O_5} = 2.88$. When the duration of one contact cycle was increased from 3 to 6 hours, the degree of conversion of vinylacetylene was reduced from 36 to 30%, and the productivity with regard to methyl vinyl ketone, from 81 to 65 g/liter of cat.–hr. Approximately the same results are obtained for cadmium tungstate. For the rest of the catalysts, increasing the duration of the contact cycle from 3 to 6 hours causes the productivity with regard to methyl vinyl ketone to fall nearly to half.

EXPERIMENTAL

Catalysts

The cadmium-calcium-phosphate catalyst was prepared through precipitation by ammonium phosphate from a mixture of cadmium nitrate and calcium acetate solutions. The precipitate was freed from soluble salts by washing and dried at 100-110°. The content of CdO and CaO in the catalyst amounted to 10 and 90 mole %, respectively.

Cadmium tungstate. This was prepared according to Leffort [16] by treatment of sodium tungstate solution with cadmium acetate:

$$Na_2WO_4 + Cd(CH_3COO)_2 \rightarrow CdWO_4 + 2NaCOOCH_3.$$

The precipitate was freed from soluble salts by washing and dried at 100-110°.

Tungsten trioxide from Kahlbaum.

Zinc oxide. Commercial zinc oxide, type M-1 (GOST 202-41).

All catalysts were compressed from powder into tablets by means of a laboratory hydraulic press.

Vinylacetylene

Technical vinylacetylene, b.p. +5°, obtained by the dimerization of acetylene, was used for the work. Its content of unsaturated compounds amounted to 99%.

The hydration of vinylacetylene was carried out in a silica tube filled with catalyst and placed in an electric furnace. The temperature of the process was measured with a thermocouple, the hot junction of which lay in the midst of the catalyst layer. The addition of water to a triple bond is an exothermic process. At the beginning of the experiment, after admitting the vinylacetylene-steam mixture to the furnace, a slight temperature rise (10-15°) was usually observed. Owing to this, the catalyst temperature before admitting the mixture to the furnace was set a little below that at which the experiment was conducted. Heat was eliminated in the given case through the heat losses of the furnace. Vinylacetylene from a gasometer (through a rheometer) and water from a buret were fed into the contact tube. The reaction products passed through a condenser, a receiver in which the aqueous condensate was collected, and traps filled with hydroxylamine hydrochloride solution for separation of methyl vinyl ketone vapor from the gas. The uncondensed vinylacetylene was collected in a gasometer over saturated sodium chloride solution. The recovery of vinylacetylene in the exhaust gas was determined through absorption by oleum in an Orsat apparatus.

The liquid reaction products consisted of two layers—water and oil; they were analyzed for their methyl vinyl ketone content by means of hydroxylamine hydrochloride. The results of the experiments on hydration of vinylacetylene are given in the table.

The methyl vinyl ketone was isolated from the water layer by rectification for the purpose of identification.

A fraction, b.p. 79-80°, d^{20}_{20} 0.8532, $n^{20}D$ 1.4110 was isolated; m.p. of semicarbazone, 138-140°.

Found: M 68.5, 68.1. C_4H_6O. Calculated : M 70.

For methyl vinyl ketone [2]: b.p. 79-80°, d^{20}_{20} 0.8520, $n^{20}D$ 1.4110; m.p. of semicarbazone, 139-140°.

No other reaction products could be isolated on investigation of the water layer.

On distillation of the oil layer (obtained from experiments done with cadmium-calcium-phosphate catalyst) a fraction with a b.p. of 65-72° (13 mm), which was a dimer of methyl vinyl ketone (2-acetyl-6-methyl-2,3-dihydropyran), and a fraction, b.p. 106° (9 mm), were obtained.

Fraction, b.p. 65-72° (13 mm).

Found %: C 67.83, 68.14; H 8.49, 8.53. M 136.8. $(C_4H_6O)_2$. Calculated %: C 68.57; H 8.57. M 140.

M.p. of semicarbazone, 174-176°.

For the methyl vinyl ketone dimer [17], b.p. 65° (13 mm): m.p. of semicarbazone, 176°.

A fraction, b.p. 106° (9 mm), $n^{20}D$ 1.5386, was also investigated.

Found M 158.5. $(C_4H_4)_3$. Calculated M 156.

Thus this fraction is apparently a trimer of vinylacetylene. Owing to its small quantity, it was not investigated in more detail.

SUMMARY

1. The process of vapor-phase hydration of vinylacetylene to methyl vinyl ketone with certain solid, mercury-free catalysts has been investigated. It has been shown that cadmium tungstate, cadmium-calcium-phosphate, tungsten trioxide, and zinc oxide may be used as catalysts for this process. Cadmium tungstate and cadmium-calcium-phosphate catalyst have the greatest selectivity with respect to methyl vinyl ketone yield.

2. It has been shown that in the vapor-phase hydration of vinylacetylene, besides methyl vinyl ketone (the main reaction product), the by-products, 2-acetyl-6-methyl-2,3-dihydropyran (in the amount of 3-4%) and a polymer of vinylacetylene (in the amount of 1-1.5%), are also formed.

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ON THE REACTION OF AMMONIA WITH METHYL α-CHLOROACRYLATE

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As Klimenko [1] and Beckurts and Otto [2] showed, in the reaction of ammonia with esters of halogen-substituted propionic acids displacement of the alkoxyl radical takes place with formation of the corresponding amides. Klimenko [1] obtained α,α-dichloropropionamide by means of the reaction of dilute ammonia with ethyl α,α-dichloropropionate at room temperature. Beckurts and Otto [2] obtained α-chloropropionamide on shaking ethyl α-chloropropionate with concentrated aqueous ammonia. On the other hand, it is known that in the reaction of ammonia with methyl methacrylate, methacrylamide is obtained in good yield [3].

It was to be expected that the reaction of ammonia with methyl α-chloroacrylate would proceed analogously according to the equation

$$CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}COOCH_3 \xrightarrow{NH_3} CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CONH_2$$

However, the attempt to obtain α-chloroacrylamide by this route showed that an entirely different reaction mechanism prevails here, and the formation of α-chloroacrylamide is not observed. The reaction proceeds with splitting off of chlorine in the form of ammonium chloride and displacement of the alkoxyl radical by the amido group. The amides thus formed polymerize so readily that they could not be isolated from the reaction mixture in monomeric form. Analysis shows that the polymers have the empirical formula $(C_3H_5O_2N)_n$ and apparently are poly-α-hydroxyacrylamides of low molecular weight

$$\left[-CH_2-\underset{\displaystyle CONH_2}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-\right]_n, \text{ where } n = 2\text{–}7.$$

Splitting off of chlorine from methyl α-chloroacrylate occurs to the same extent on reaction with either concentrated aqueous or dry, gaseous ammonia at either room temperature or lower ones (from 0 to -25°), whereupon the final polymer isolated from aqueous solutions has the same composition, irrespective of the conditions of the reaction with ammonia. The formation of polymers occurs both in the absence and in the presence of an inhibitor (hydroquinone). Similarly, both with aqueous and with gaseous ammonia under the same conditions (from 0 to -25°), splitting off of chlorine from methyl α, β-dichloropropionate occurs. In both cases, instead of the expected α, β-dichloropropionamide, a polymer of low molecular weight, having the same composition as that obtained in the reaction of ammonia with methyl α-chloroacrylate, $(C_3H_5O_2N)_n$, is isolated as the final product. The mechanism of the reaction of ammonia with methyl α-chloroacrylate and methyl α, β-dichloropropionate may be represented by the scheme

$$CH_2Cl{-}CHCl{-}COOCH_3 \xrightarrow[-HCl]{NH_3} CH_2{=}CCl{-}COOCH_3 \xrightarrow{NH_3}$$

$$\longrightarrow \left[-CH_2-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CONH_2}{\overset{|}{C}}}}-\right]_n \xrightarrow{NH_4OH} \left[-CH_2-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CONH_2}{\overset{|}{C}}}}-\right]_n$$

The reaction of splitting off of chlorine from esters of α-chloroacrylic and α, β-dichloropropionic acids have not been described in the literature up to now. Apparently it is a general reaction, characteristic of esters of saturated aliphatic acids containing chlorine in the α, β-position.

EXPERIMENTAL

Methyl α-chloroacrylate was prepared according to Marvel [4] by dehydrochlorination of methyl α, β-dichloropropionate in the presence of freshly distilled quinoline. The reaction mixture was heated to boiling, and methyl α-chloroacrylate was distilled off at 57-59° (55 mm). After distillation through a column containing metallic (copper) packing the methyl α-chloroacrylate had a b.p. of 58° (55 mm), d^{20}_4 1.1892, $n^{20}D$ 1.4400.

Methyl α, β-dichloropropionate was prepared by chlorination of methyl acrylate [5,6].

a) Reaction of aqueous ammonia with methyl α-chloroacrylate at room temperature. To 120.5 g of methyl α-chloroacrylate in a liter flask was added 1.2 g of hydroquinone and 300 ml of aqueous ammonia. The mixture was periodically shaken at room temperature until it became homogeneous. (With vigorous shaking, the reaction continued for 1–1.5 hours with negligible heating). The solution was concentrated in vacuo, and a brown, resinous mass was formed; on fractional crystallization of an aqueous solution of this mass crystals were isolated, which decomposed, without melting, at a temperature over 300°. The crystals gave a reaction for chlorine with $AgNO_3$ and evolved gaseous ammonia on heating with alkali.

Found %: N 26.81; Cl 65.80. M 56. NH_4Cl. Calculated %: N 26.1; Cl 66.3. M 53.5.

Removal of the ammonium chloride was accomplished by careful, gradual solution of the viscous, resinous reaction mass in minimum quantities of water, followed by precipitation with a 5-fold quantity of methyl alcohol. Thereupon the ammonium chloride passed into the water-methanol mixture, and the resin was precipitated, gradually being freed from ammonium chloride. The operation was carried out until there was no reaction for chlorine (with $AgNO_3$). In all, 52.9 g of ammonium chloride (98.9%, calculated on the basis of the original methyl α-chloroacrylate) was removed.

After drying to constant weight in vacuo at room temperature a yellowish-brown polymer (85.2 g, 97.9%) was obtained, which formed a colored, transparent film on evaporation of the solvent. The polymer was readily soluble in water, less so in alcohol, and quite insoluble in other organic solvents (benzene, ether, acetone, dioxan). Softening point in a capillary, 71°.

Found %: C 41.95; H 5.97; N 16.40; OH 96.9 (after Verley). M 600 (cryoscop.). $(C_3H_5O_2N)_7$. Calculated %: C 41.38; H 5.75; N 16.10. n = 7, M 609.

b) Reaction of gaseous ammonia with methyl α-chloroacrylate. For a more detailed study of the mechanism of the reaction of methyl α-chloroacrylate and ammonia, methyl α-chloroacrylate was saturated with gaseous ammonia at a temperature from 0 to -5°. After cooling to 0 to -5°, 82 g of methyl α-chloroacrylate was strongly saturated for 2 hours with ammonia gas from a cylinder, dried with calcium chloride. The flask containing the reaction products was left in solid carbon dioxide overnight. From the reaction mixture, after standing at room temperature, a copious quantity of fine crystals (34.0 g, 92%) of ammonium chloride separated out.

Found %: N 25.63; Cl 66.37. NH_4Cl. Calculated %: N 26.1; Cl 66.3.

After elimination of the ammonium chloride the mother liquor was treated with alcohol, from which were isolated white crystals (4 g), m.p. 122°, which gave a negative reaction for chloride ion.

Found %: C 37.51; H 5.40; N 22.16; Cl 18.61. M (cryoscop.) 181.1. $C_6H_{10}O_2N_3Cl$. Calculated %: C 37.60; H 5.22; N 21.93; Cl 18.53. M 191.5.

The structure of this substance was established.

After elimination of the ammonium chloride and the crystalline substance with a m.p. of 122° the resinous reaction mass was freed from traces of ammonium chloride by the method described above. The remainder of the polymer amounted to 54 g. The polymer was readily soluble in water, less so in alcohol, and quite insoluble in organic solvents (benzene, ether, acetone, dioxan).

Found %: C 41.08; H 5.97; N 16.00. M (cryoscop.) 282.2. $(C_3H_5O_2N)_3$. Calculated %: C 41.38; H 5.75; N 16.10. M 261.

c) Reaction of ammonia with methyl α-chloroacrylate at -20 to -25° in anhydrous chloroform. On the assumption that splitting off of chlorine would occur to a lesser extent under milder conditions, methyl α-chloroacrylate was saturated with ammonia in anhydrous chloroform solution at a temperature from -20 to -25°. Into the reaction mixture, which consisted of 30.0 g of methyl α-chloroacrylate and 15 ml of anhydrous chloroform (cooled to -20 to -25° in an acetone-dry ice mixture), ammonia gas from a cylinder, dried with calcium chloride, was passed for 3 hours. A white, crystalline precipitate (12.3 g) of ammonium chloride separated out from the reaction mixture at room temperature. The resinous reaction mixture was repeatedly dissolved in water and precipitated with acetone until all traces of ammonium chloride were eliminated (reaction with $AgNO_3$). Eighteen and seven-tenths g of the polymer was isolated.

Found %: C 40.95; H 6.05; N 16.38. M (cryoscop.) 182. Hydroxyl groups (after Verley) 99.6%. $(C_3H_5O_2N)_2$. Calculated %: C 41.13; H 5.75; N 16.10. M 174.

d) Reaction of ammonia with methyl-α, β-dichloropropionate. It was of interest to establish the character of the reaction of ammonia with methyl α,β-dichloropropionate. Dry ammonia gas from a cylinder was rapidly passed for 2 hours into a flask containing 100 g of methyl α, β-dichloropropionate at a temperature from 0 to -5°. At room temperature 58.0 g of crystals separated out, and sublimed, without melting, at a temperature over 300°.

Found %: N 26.24; Cl 65.98. NH_4Cl. Calculated %: N 26.10; Cl 66.30.

The resinous reaction mass was repeatedly dissolved in the minimum quantities of distilled water and precipitated with acetone until all traces of ammonium chloride were eliminated. Fifty-two g of a polymer, having a softening point in a capillary, of 102°, and the same properties with respect to solubility as the polymers described above, was isolated.

Found %: C 41.07; N 16.09; H 5.83. M (cryoscop.) 169.5. Hydroxyl groups (after Verley) 98.6%. $(C_3H_5O_2N)_2$. Calculated %: C 41.38; N 16.10; H 5.75. M 174.

SUMMARY

1. It has been established that on treatment of methyl α-chloroacrylate with aqueous ammonia, both at room temperature and at lower temperatures (to 0°), splitting off of chlorine occurs with formation of ammonium chloride and a polymer of low molecular weight. Splitting off of chlorine also occurs in the reaction of methyl α-chloroacrylate with ammonia gas at these and lower temperatures, even if the reaction takes place in a dry chloroform medium.

2. It has been shown that splitting off of chlorine also occurs when aqueous and gaseous ammonia react with methyl α, β-dichloropropionate to form the same final products.

3. A mechanism is suggested for the reactions of methyl α-chloroacrylate and methyl α, β-dichloropropionate with ammonia.

4. It has been shown that the polymer formed is a poly-α-hydroxyacrylamide of low molecular weight.

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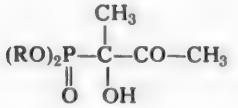
REACTION OF DIALKYL PHOSPHOROUS ACIDS WITH ALDEHYDES AND KETONES

ESTERS OF 1-HYDROXY-1-ACETOETHYLPHOSPHONIC AND 2-HYDROXY-4-KETO-2-AMYLPHOSPHONIC ACIDS

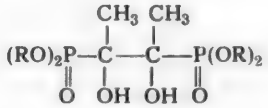
V. S. Abramov, L. Sh. Belokon' and F. I. Makhmutova

Expanding our previous studies in this field [1], we made a systematic investigation of the condensation of dialkyl phosphorous acids with biacetyl and acetylacetone. The formation of two products—either with one or with two carbonyl groups—could be expected in the condensation of dialkyl phosphorous acids with diketones.

In α-diketones (biacetyl) the carbonyl groups, exerting a mutual influence on each other, enhance polarization. This circumstance should facilitate the condensation of dialkyl phosphorous acids with the first carbonyl group in biacetyl with the formation of substance (I). The reaction of the second carbonyl group with a second molecule of the dialkyl phosphorous acid should depend on the influence exerted by the phosphono group, found in the molecule, on the reactivity of the molecule and the spatial possibilities arising in this connection. Substance (II) should be formed in the case of successful reaction.



(I)



(II)

Our investigation revealed that the condensation of dialkyl phosphorous acids with an equimolar amount of biacetyl proceeds well, without a catalyst, if the reaction mixture is heated on the water bath, and is complete in 10—12 hours. The constants of the crude products obtained here are very close to the constants of the vacuum-distilled products. The obtained esters can be vacuum-distilled without decomposition and have a constant boiling point, in contrast to the condensation products of dialkyl phosphorous acids with monoaldehydes and ketones [2]. The stability of the obtained products (I) to heat can be explained by the possible formation of hydroxyl groups as the result of hydrogen bonding with both the oxygen of the phosphono group and the oxygen of the carbonyl group. Evidently, hydrogen bonding with the oxygen of the carbonyl group predominates and makes the phosphorus—carbon bond stable, and consequently the molecule as a whole stable.

The synthesized esters of 1-hydroxy-1-acetoethylphosphonic acid are listed in Table 1.

The esters of 1-hydroxy-1-acetoethylphosphonic acid are colorless sirupy liquids, practically without odor.

The experiments on the condensation of 2 moles of dialkyl phosphorous acids with 1 mole of biacetyl proved unsuccessful. When the reaction products were subjected to fractional distillation we isolated the unreacted dialkyl phosphorous acid (about 50% of that taken), the corresponding ester of 1-hydroxy-1-acetoethylphosphonic acid (67—78%), and a small amount of residue, from which it proved impossible to isolate any definite compound.

TABLE 1

Esters of 1-Hydroxy-1-acetoethylphosphonic Acid $(RO)_2P(O)-C(CH_3)(OH)-CO-CH_3$

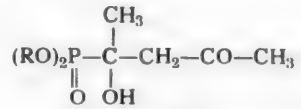
Experiment No.	R	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Yield (in %)	P (in %) found	P (in %) calculated
1	CH_3	116° (4mm)	1.4530	1.2391	42.71	42.31	51.0	15.80, 15.93	15.81
2	C_2H_5	120 (4)	1.4450	1.1403	51.05	51.55	55.0	13.76, 13.73	13.84
3	iso-C_3H_7	115 (3)	1.4410	1.1211	60.32	60.78	86.5	12.36, 12.49	12.30
4	C_4H_9	142 (4)	1.4480	1.0641	70.52	70.02	84.0	11.22, 11.11	11.07
5	iso-C_4H_9	131 (3)	1.4430	1.0513	70.63	70.02	86.0	10.91, 11.29	11.07

TABLE 2

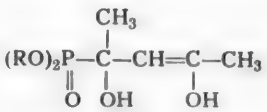
Esters of 2-Hydroxy-4-keto-2-amylphosphonic Acid $(RO)_2P(O)-C(CH_3)(OH)-CH_2CO-CH_3$

Experiment No.	R	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated (IV)	MR_D calculated (III)	Unsaturation (%)	Yield (in %)	P (in %) found	P (in %) calculated
1	CH_3	107—108° (3mm)	1.4550	1.1677	48.78	48.14	47.08	40.2	8	14.87, 14.82	14.76
2	C_2H_5	114—115 (3)	1.4450	1.1019	57.48	57.38	56.33	34.0	27	13.25, 13.12	13.02
3	iso-C_3H_7	115—116 (2)	1.4400	1.0542	66.50	66.61	65.56	35.6	14	11.53, 11.82	11.65
4	C_4H_9	139—140 (3)	1.4490	1.0278	77.10	75.80	74.80	30.0	18	10.68, 10.72	10.54
5	iso-C_4H_9	137—138 (4)	1.4470	1.0153	77.30	75.80	74.80	40.0	21	10.97, 10.77	10.54

The condensation of dialkyl phosphorous acids with acetylacetone should proceed with the formation of esters of 2-amylphosphonic acid derivatives. The condensation of a dialkyl phosphorous acid with one carbonyl group of acetylacetone in its carbonyl form yields the ester of 2-hydroxy-4-keto-2-amylphosphonic acid with structure (III), while reaction with the enol form of acetylacetone yields the ester of 2,4-dihydroxy-2-penten--3-yl-phosphonic acid with structure (IV).



(III)



(IV)

It is also possible for dialkyl phosphorous acids to add to the double bond of the enolic form of acetylacetone, but then substance (III) should be obtained. In both cases reaction leads to the same product, having two tautomeric forms that are found in equilibrium.

The condensation of dialkyl phosphorous acids with an equimolar amount of acetylacetone proceeds, in the absence of a catalyst, with somewhat more difficulty than in the case of biacetyl. Here fractional distillation of the reaction products gave the corresponding esters in low yields, shown in Table 2.

Two values are given in Table 2 for the calculated molecular refraction: (IV)—for the enolic form, and (III)—for the ketonic form. When the found molecular refractions are compared with the calculated, we find that they lie closer to (IV). The unsaturation of the obtained esters, determined by titration with bromate-bromide solution, permits concluding that the esters of 2-hydroxy-4-keto-2-amylphosphonic acid are enolized to the extent of 30—40%.

An attempt to determine the amount of carbonyl group using phenylhydrazine proved unsuccessful.

The condensation of 2 moles of dialkyl phosphorous acid with 1 mole of acetylacetone failed to give a product with two phosphono groups.

EXPERIMENTAL

Equimolar amounts of dialkyl phosphorous acid and either biacetyl or acetylacetone were mixed; the density and the refractive index of the mixture were determined. Then the mixture was heated in ampules on the water bath. The refraction was measured at periodic intervals: the reaction was considered ended when the refraction remained constant. The products were fractionally distilled in vacuo. The results are given in Tables 1 and 2.

SUMMARY

1. It was shown that dialkyl phosphorous acids condense with both biacetyl and acetylacetone. The corresponding esters—the products of the condensation of equimolar amounts of the reactants—were obtained.

2. The esters of 1-hydroxy-1-acetoethylphosphonic acid are relatively stable to heat (distillation), which is explained by hydrogen bonding of the 1-hydroxy group with the oxygen of the carbonyl group.

3. The esters of 2-hydroxy-2-keto-4-amylphosphonic acid showed 30—40% enolization.

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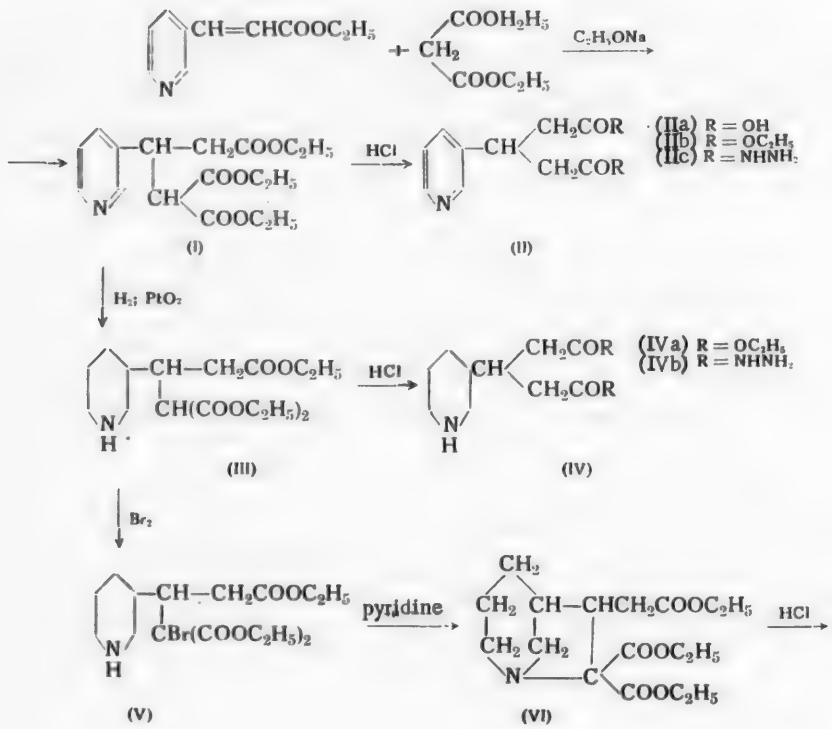
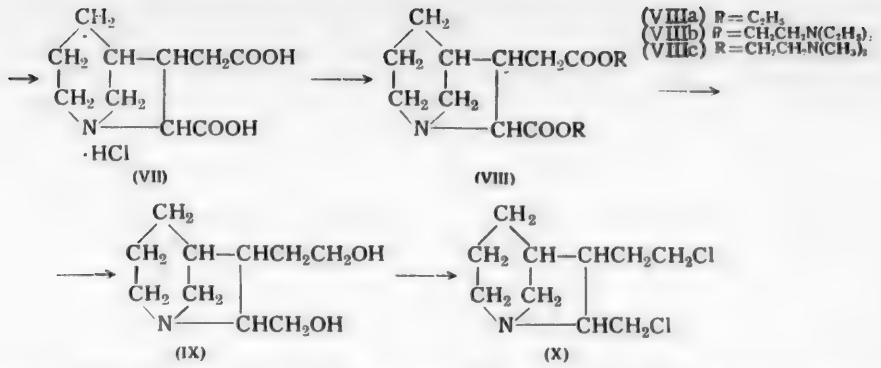
SYNTHESIS OF 6-CARBOXYMETHYL-1-AZABICYCLO (3.2.1) OCTANE-7-CARBOXYLIC ACID AND SOME OF ITS DERIVATIVES

V. Ia. Furshtatova, E. E. Mikhlina and M. V. Rubtsov

A whole series of studies [1–3] has been devoted to the synthesis and biological investigation of quinuclidine (1-azabicyclo (2.2.2) octane) derivatives. At the same time the bicyclic system 1-azabicyclo (3.2.1) octane, isomeric with quinuclidine, has been studied but slightly. Here it is necessary to mention the preparation of only a limited number of 6-monosubstituted 1-azabicyclo (3.2.1) octanes [4]. Disubstituted octanes of the indicated structure were not obtained. In view of the fact that a number of biologically active compounds were found among the 2,3-disubstituted quinuclidine derivatives synthesized by us, it seemed of interest to synthesize the isomeric 6,7-disubstituted 1-azabicyclo (3.2.1) octane derivatives and then compare the biological and chemical properties of the two series of isomeric compounds.

In this paper we describe the synthesis of 6-carboxymethyl-1-azabicyclo (3.2.1) octane-7-carboxylic acid and some of the compounds derived from this acid. The synthesis was accomplished by the following scheme:





The reaction of the ethyl ester of β-(3-pyridyl) acrylic acid with malonic ester in the presence of an equivalent amount of sodium alcoholate at room temperature or with short heating gave the ethyl ester of β-dicarbethoxymethyl-β-(3-pyridyl)propionic acid (I) in nearly quantitative yield. The boiling of (I) with hydrochloric acid gave β-(3-pyridyl)glutaric acid (IIa), which when heated with an alcohol solution of hydrogen chloride was converted to the diethyl ester (IIb). The dihydrazide (IIc) was obtained from the latter.

In accordance with the indicated scheme, ester (I) was further reduced in the presence of platinum catalyst (of the Adams type) to the ethyl ester of β-dicarbethoxymethyl-β-(3-piperidyl)propionic acid (III). Ester (III), readily soluble in organic solvents and hydrochloric acid, when heated in vacuo (0.1 mm) at 160° is converted to an undistillable solid mass, insoluble in ether, benzene, chloroform and hydrochloric acid. Apparently, here compounds of lactam character are formed under the influence of high temperature. This postulation is supported by the fact that when heated with concentrated hydrochloric acid the solid mass goes into solution. Here the hydrochloride of β-(3-piperidyl)glutaric acid is formed, from which we obtained the corresponding diethyl ester (IVa). The latter was also synthesized by heating ester (III) with hydrochloric acid and subsequent esterification of the resulting diacid. Diester (IVa) was converted to the dihydrazide (IVb).

Ester (III) was also converted to its N-acetyl derivative—the ethyl ester of β-dicarbethoxymethyl-β-(N-acetyl-3-piperidyl)propionic acid.

To synthesize the substituted azabicyclooctane derivatives, ester (III) was treated with bromine in chloroform solution. This gave the ethyl ester of β-dicarbethoxybromomethyl-β-(3-piperidyl)propionic acid (V). The latter when heated with pyridine gave the diethyl ester of 6-carbethoxymethyl-1-azabicyclo (3.2.1)octane-7,7-dicarboxylic acid (VI). Long heating of ester (VI) with hydrochloric acid led to the hydrochloride of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid (VII). Three different methods were used to isolate the free acid: treatment of the hydrochloride of the acid with moist silver oxide and subsequent decomposition of the silver salt of the acid with hydrogen sulfide, treatment of the hydrochloride of the acid with the calculated amount of alcoholic ammonia solution, and long boiling of a water solution of the ethyl ester of 6-carbethoxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid. 6-Carboxymethyl-1-azabicyclo(3.2.1)-octane-7-carboxylic acid exists in two forms—the anhydrous form with m.p. 237°, and the crystallohydrate with m.p. 82°. The latter when heated in vacuo over phosphorus pentoxide at 60°, and also when boiled in anhydrous alcohol, loses water and is transformed to the anhydrous acid with m.p. 237°, which in the air again forms the crystallohydrate.

The heating of hydrochloride (VII) with an alcohol solution of hydrogen chloride gave the diethyl ester of 6-carboxymethyl-1-azabicyclo(3.2.1)octane-7-carboxylic acid (VIIIa). Diester (VIIIa) is also formed by reacting acid (VII) with thionyl chloride, followed by heating the obtained dichloride with alcohol. The reaction of the hydrochloride of the dichloride of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid with diethylaminoethanol and dimethylaminoethanol gave the corresponding esters (VIIIb) and (VIIIc). Diester (VIIIa) was reduced with aluminum lithium hydride to 6-(β-hydroxyethyl)-7-hydroxymethyl-1-azabicyclo (3.2.1)octane (IX). Diol (IX) with thionyl chloride was converted to 6-(β-chloroethyl)-7-chloromethyl-1-azabicyclo (3.2.1)octane (X).

EXPERIMENTAL

Ethyl β-dicarbethoxymethyl-β-(3-pyridyl)propionate (I). To an alcohol solution of sodium ethylate prepared from 5.6 g of sodium metal and 80 ml of anhydrous alcohol, was added 39 g of malonic ester and 43 g of ethyl β-(3-pyridyl)acrylate. The reaction mixture was stirred thoroughly until homogeneous, after which it was heated for 1 hour at 60–63°. The cooled solution was poured into 400 ml of water, containing 15.7 g of acetic acid. The deposited oil was extracted with ether. The ether extract was washed several times with water and then dried over sodium sulfate. Removal of the ether by distillation left 76.5 g (93.5%) of a viscous oily substance, being the ethyl ester of β-dicarbethoxymethyl-β-(3-pyridyl)propionic acid; b.p. 167–168° (0.2 mm). The substance is readily soluble in organic solvents and insoluble in water; $n^{18}D$ 1.4791.

Found %: N 4.15, 4.09. $C_{17}H_{23}O_6N$. Calculated %: N 4.15.

To obtain the hydrochloride an ether solution of the above substance was treated with an alcohol solution of hydrogen chloride until acid to Congo. The deposited oil crystallized on cooling. M.p. 119–120° (from a mixture of alcohol and ether).

Found %: C 54.39, 54.60; H 6.53, 6.26; Cl 9.85, 9.74; N 3.76. $C_{17}H_{23}O_6N \cdot HCl$. Calculated %: C 54.60; H 6.42; Cl 9.46; N 3.75.

β-(3-Pyridyl)glutaric acid (IIa). A mixture of 7 g of ethyl β-dicarbethoxymethyl-β-(3-pyridyl)propionate and 70 ml of concentrated hydrochloric acid was refluxed for 10 hours. The hydrochloric acid solution was concentrated in vacuo, and the residue was dried by treating with anhydrous alcohol three times with removal of the alcohol by distillation between additions. We obtained 4.6 g (100%) of the hydrochloride of the indicated acid. The compound was obtained as colorless crystals, readily soluble in water, difficultly soluble in hot alcohol, and insoluble in cold alcohol, acetone and ether. It was recrystallized from alcohol; m.p. 134.5–135.5° (decompn.).

Found %: C 48.62; H 5.47; N 5.41; Cl 14.45. $C_{10}H_{11}O_4N \cdot HCl$. Calculated %: C 48.88; H 4.88; N 5.7; Cl 14.47.

Ethyl β-(3-pyridyl)glutarate (IIb). A mixture of 4.6 g of β-(3-pyridyl)glutaric acid hydrochloride and 70 ml of a 5% alcohol solution of hydrogen chloride was refluxed for 4 hours. The alcohol was removed in vacuo, and the residue was treated with 50% potash solution and extracted with ether. The ether solution was dried over potash. After removal of the solvent the residue was vacuum-distilled. B.p. 147–149° (0.25 mm). Colorless viscous liquid, soluble in organic solvents and insoluble in water.

Found %: C 62.97, 63.08; H 7.02, 7.09; N 5.48, 5.24. $C_{14}H_{19}O_4N$. Calculated %: C 63.40; H 7.17; N 5.28.

β-(3-Pyridyl)glutaric acid dihydrazide (IIc). A solution of 0.6 g of ethyl β-(3-pyridyl)glutarate and 0.6 ml of hydrazine hydrate in 5 ml of alcohol was heated at the boil for 4 hours. The cooled solution deposited a precipitate, which was filtered and washed with ether. Yield 0.51 g (95.5%). The dihydrazide was obtained as colorless crystals, readily soluble in water and alcohol, and insoluble in ether. M.p. 149–150° (decompn.).

Found %: C 50.29; H 5.95; N 29.42, 29.21. $C_{10}H_{16}O_2N_6$. Calculated %: C 50.63; H 6.33; N 29.52.

Ethyl β-dicarbethoxymethyl-β-(3-piperidyl)propionate (III). A solution of 40 g of ethyl β-dicarbethoxymethyl-β-(3-pyridyl)propionate hydrochloride in 300 ml of anhydrous alcohol was hydrogenated in the presence of 1 g of platinum oxide at room temperature. When the theoretical amount of hydrogen had been absorbed the catalyst was filtered and the filtrate was evaporated in vacuo. The residue resembled caramel. The yield of the hydrochloride of (III) was quantitative. The free base (III), isolated by treating the hydrochloride with 50% potash solution, when heated in vacuo (0.1 mm, 160–200°) was converted to an undistillable solid mass, insoluble in ether, benzene and chloroform. This mass is apparently a lactam type of compound, since it dissolves in hydrochloric acid only when heated.

To characterize the reduction product we synthesized the ethyl ester of β-dicarbethoxymethyl-β-(N-acetyl-3-piperidyl)propionic acid. To obtain this compound we heated the free base (III) with 5 parts of

acetic anhydride for 1 hour on the boiling water bath. The acetic anhydride was vacuum-distilled, the residue was dissolved in ether, and the ether solution was washed with aqueous sodium bicarbonate solution and then dried over potash. After distilling off the solvent the residue was vacuum-distilled. B.p. 215° (0.5 mm). The compound is an exceedingly viscous greenish liquid, readily soluble in organic solvents, and insoluble in water.

Found %: C 59.38; H 8.29; N 3.93. $C_{19}H_{31}O_7N$. Calculated %: C 59.22; H 8.05; N 3.64.

Diethyl β-(3-piperidyl)glutarate (IVa). A mixture of 2 g of ethyl β-dicarbethoxymethyl-β-(3-piperidyl)-propionate hydrochloride and 20 ml of concentrated hydrochloric acid was refluxed for 5 hours. Then the solution was evaporated in vacuo, and the residue was dried by treating with anhydrous alcohol 3 times and removing the alcohol after each treatment. To the obtained β-(3-piperidyl)glutaric acid hydrochloride was added 20 ml of an 11% alcohol solution of hydrogen chloride and the reaction mass was heated at the boil for 2 hours. The alcohol was vacuum-distilled, and the residue was treated with 50% potash solution and then extracted with ether. The ether solution was dried over potash. After removal of the ether the substance was vacuum-distilled. B.p. 133–134° (0.4 mm). Yield 1.2 g (87.5%). The diester is a colorless mobile liquid, readily soluble in water and organic solvents; $n^{17}D$ 1.4718.

Found %: C 61.57, 61.60; H 9.08, 9.32; N 5.14. $C_{14}H_{25}O_4N$. Calculated %: C 61.99; H 9.22; N 5.20.

β-(3-Piperidyl)glutaric acid dihydrazide (IVb). A solution of 0.47 g of the diethyl ester of β-(3-piperidyl)-glutaric acid and 0.5 ml of hydrazine hydrate in 5 ml of alcohol was heated at the boil for 4 hours. After distilling off the alcohol and excess hydrazine hydrate the residue crystallized. The crystals were rubbed with ether and filtered. Yield 0.38 g (90.5%). The dihydrazide was obtained as colorless crystals, soluble in water and alcohol, and insoluble in ether. M.p. 148–150° (decompn.).

Found %: C 49.18, 49.27; H 8.63, 8.70. $C_{10}H_{21}O_2N_5$. Calculated %: C 49.32; H 8.64.

Diethyl 6-carbethoxymethyl-1-azabicyclo (3.2.1)octane-7,7-dicarboxylate (VI). Ethyl β-dicarbethoxy-methyl-β-(3-piperidyl)propionate hydrochloride, obtained by the reduction of 40 g of the corresponding pyridine derivative, was dissolved in 125 ml of dry chloroform. To the chloroform solution was added in 8 hours a solution of 17.3 g of bromine in 130 ml of dry chloroform at room temperature and with good stirring. The solution decolorized completely in the next 12–14 hours. Then the chloroform was removed in vacuo, the residue was dissolved in 136 ml of water, the aqueous solution was treated with an equal volume of 50% potash solution, and the resulting oil was extracted with ether. The ether solution of the β-dicarbethoxy-bromomethyl-β-(3-pyridyl)propionate (V) was evaporated in vacuo and the remaining oil was boiled for 2 hours with 360 ml of pyridine. Here the reaction mass assumed a dark-brown color. After distilling off the pyridine the remaining dark-brown viscous oil was treated with 50% potash solution and the diethyl ester of 6-carbethoxymethyl-1-azabicyclo (3.2.1)octane-7,7-dicarboxylic acid was extracted with ether. The ether solution was dried over potash, the ether was distilled off, and the residue was vacuum-distilled. B.p. 126–128° (0.1 mm). Yield 29.35 g (80.3%). Colorless mobile liquid, readily soluble in water and organic solvents.

$n^{18}D$ 1.4777, d^{18}_4 1.130, MR_D 85.37; calculated 85.20.

Found %: N 4.19. $C_{17}H_{27}O_6N$. Calculated %: N 4.11.

6-Carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid hydrochloride (VII). A mixture of 15.3 g of diethyl 6-carbethoxymethyl-1-azabicyclo (3.2.1)octane-7,7-dicarboxylate and 150 ml of concentrated hydrochloric acid was heated under reflux for 20 hours. Then the hydrochloric acid solution was decolorized with charcoal and evaporated on the water bath to incipient crystallization. Cooling gave the hydrochloride of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid as lustrous white plates, which were filtered and washed well with acetone. Yield 10.2 g (92.5%). White crystalline powder, readily soluble in water, difficultly soluble in hot alcohol, and insoluble in cold alcohol, acetone and ether. M.p. 232–235° (decompn.).

Found %: C 48.02, 47.77; H 6.28, 6.44; Cl 13.91, 13.78. $C_{10}H_{16}O_4NCl$. Calculated %: C 48.10; H 6.42; Cl 14.22.

6-Carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid. a) Moist silver oxide, prepared from 1.93 g of silver nitrate, was added to a solution of 0.5 g of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid hydrochloride in 7 ml of water, and the resulting suspension was shaken for 16 hours. Then the reaction mass was diluted with 40 ml of water, brought to a boil, filtered, and the precipitate washed 4 times

with 10 ml portions of hot water. The filtrate was saturated with hydrogen sulfide, the silver sulfide was filtered, and the colorless aqueous solution of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid was evaporated in vacuo to dryness. We obtained 0.3 g of the acid (70.5%) as colorless crystals, readily soluble in water, difficultly soluble in alcohol, and insoluble in ether and benzene. M.p. 237° (decompn.).

b) A solution of 0.2 g of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid hydrochloride in 8 ml of anhydrous alcohol was prepared by heating at the boil. Then the solution was treated with 1.515 ml of alcoholic ammonia solution, containing 0.01365 g of ammonia, and the whole allowed to stand for 60 hours. Colorless crystals of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid deposited during this time. Yield 0.1 g (62.6%). M.p. 237° (decompn.).

Found %: C 55.82, 55.76; H 7.31, 7.00. $C_{10}H_{15}O_4N$. Calculated %: C 56.34; H 7.04.

In air 6-carboxymethyl-1-azabicyclo(3.2.1)octane-7-carboxylic acid is converted to the crystallohydrate, containing 1/2 H_2O, with m.p. 82°.

Found %: C 53.92, 53.66; H 7.61, 7.54. $C_{10}H_{15}O_4N \cdot 1/2H_2O$. Calculated %: C 54.00; H 7.26.

The crystallohydrate can again be converted to the anhydrous acid with m.p. 237° by drying in vacuo (15 mm) over phosphorous pentoxide at 60°, and also by boiling with anhydrous alcohol.

c) A solution of 2 g of ethyl 6-carbethoxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylate in 20 ml of water was heated at the boil for 40 hours. Evaporation of the aqueous solution in vacuo gave 1.4 g of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid as the crystallohydrate. M.p. 82°.

Ethyl 6-carbethoxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylate (VIIIa). a) A mixture of 10 g of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid hydrochloride and 100 ml of thionyl chloride was heated on the water bath at 60–65° for 4 hours. The excess thionyl chloride was removed in vacuo. Its complete removal was achieved by adding anhydrous benzene twice with removal of the benzene by vacuum-distillation each time. To the obtained hydrochloride of the acid dichloride was added 100 ml of anhydrous alcohol. The alcohol solution was heated at the boil for 3 hours. The alcohol was vacuum-distilled, the residue was treated with 50% potash solution, and the obtained oil was extracted with ether. The ether solution was dried over potash. The ether was distilled off and the substance was vacuum-distilled. We obtained 9.9 g (91%) of ethyl 6-carbethoxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylate with b.p. 130–131° (0.35 mm). The compound is a yellowish oil, readily soluble in organic solvents and in water (with opalescence); $n^{18}D$ 1.4774.

b) A mixture of 10 g of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid hydrochloride and 100 ml of an 11% alcohol solution of hydrogen chloride was heated at the boil for 8 hours. Treatment in the same manner as described in (a) gave 9.2 g (85.3%) of the diester. B.p. 130–131° (0.35 mm), $n^{18}D$ 1.4774.

Found %: C 62.29; H 8.37; N 4.95. $C_{14}H_{23}O_4N$. Calculated %: C 62.45; H 8.55; N 5.21.

Di-(diethylaminoethyl) ester of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid (VIIIb). A mixture of 2 g of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid hydrochloride and 20 ml of thionyl chloride was heated for 8 hours at 60–65°. On conclusion of reaction the excess thionyl chloride was vacuum-distilled, the residue was treated with 20 ml of diethylaminoethanol, and the mixture was heated for 3 hours at 85–90°. The unreacted diethylaminoethanol was distilled off, the obtained ester hydrochloride was treated with 50% potash solution, and the resulting oil was extracted with ether. After drying the ether solution over potash the solvent was distilled off and the residue was vacuum-distilled. We obtained 2 g (60.8%) of the di-(diethylaminoethyl) ester of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid with b.p. 186–188° (0.1 mm). The compound is an oil, readily soluble in organic solvents and in water; $n^{17.3}D$ 1.4855.

Found %: C 63.87, 64.15; H 9.88, 9.93; N 10.26. $C_{22}H_{41}O_4N_3$. Calculated %: C 64.23; H 9.98; N 10.22.

Di-(dimethylaminoethyl) ester of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid (VIIIc). To the hydrochloride of the dichloride of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid, obtained, in the same manner as described above, from 2 g of the hydrochloride of the acid, was added 20 ml of dimethylaminoethanol. After suitable treatment we obtained 1.8 g (63%) of the di-(dimethylamino-

ethyl) ester of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid as a yellow viscous oil, readily soluble in organic solvents and in water. B.p. 178–180° (0.1 mm); $n^{17.3}D$ 1.4855.

Found %: N 11.77, 11.53. $C_{18}H_{33}O_4N_3$. Calculated %: N 11.83.

6-(β-Hydroxyethyl)-7-hydroxymethyl-1-azabicyclo (3.2.1)octane (IX). A solution of 2 g of ethyl 6-carbethoxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylate in 25 ml of absolute ether was added with stirring to 1 g of aluminum lithium hydride in 25 ml of absolute ether. The reaction mass was heated at the boil for 1 hour. Then 1.85 ml of water was added with good cooling and stirring, and the obtained precipitate of aluminum and lithium hydroxides was filtered and washed well on the filter with chloroform. The ether and chloroform extracts were combined and dried over potash. Removal of the solvents by vacuum-distillation gave 1.3 g (95%) of 6-(β-hydroxyethyl)-7-hydroxymethyl-1-azabicyclo (3.2.1)octane. Colorless viscous oil, readily soluble in water and in chloroform, and more difficultly soluble in ether. B.p. 154° (0.4 mm).

Found %: C 64.75, 64.54; H 9.88, 10.00; N 7.51, 7.16. $C_{10}H_{19}O_2N$. Calculated %: C 64.86; H 10.26; N 7.56.

6-(β-Chloroethyl)-7-chloromethyl-1-azabicyclo (3.2.1)octane (X). To the hydrochloride of 6-(β-hydroxyethyl)-7-hydroxymethyl-1-azabicyclo (3.2.1)octane, obtained from 3.5 g of the free base, was added 30 ml of dry chloroform, followed by the gradual addition of 28 ml of thionyl chloride with cooling. The solution was heated at the boil for 1 hour. The chloroform and excess thionyl chloride were removed in vacuo. The residue was treated with 50% potash solution and the 6-(β-chloroethyl)-7-chloromethyl-1-azabicyclo (3.2.1)octane was extracted with chloroform. The chloroform solution was dried over potash. After removal of the chloroform the dichloro compound was vacuum-distilled. Yield 3.3 g (77.5%). B.p. 105–106° (0.15 mm). The dichloro compound is a colorless mobile liquid, readily soluble in water and organic solvents. On long standing the liquid gradually becomes turbid, apparently due to the formation of a polymer with the properties of a quaternary salt.

Found %: C 54.35; H 7.66. $C_{10}H_{17}NCl_2$. Calculated %: C 54.05; H 7.66.

SUMMARY

Starting with the ethyl ester of β-(3-pyridyl)acrylic acid, the synthesis of 6-carboxymethyl-1-azabicyclo-(3.2.1)octane-7-carboxylic acid was accomplished via the following route: ethyl ester of β-dicarbethoxymethyl-β-(3-pyridyl)propionic acid to the ethyl ester of β-dicarbethoxymethyl-β-(3-piperidyl)propionic acid to the ethyl ester of β-dicarbethoxybromomethyl-β-(3-piperidyl)propionic acid to the diethyl ester of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7,7-dicarboxylic acid.

Together with the indicated compounds, we prepared the diethyl ester of 6-carboxymethyl-1-azabicyclo-(3.2.1)octane-7-carboxylic acid, di-(diethylaminoethyl) and di-(dimethylaminoethyl) esters of 6-carboxymethyl-1-azabicyclo (3.2.1)octane-7-carboxylic acid, 6-(β-hydroxyethyl)-7-hydroxymethyl-1-azabicyclo-(3.2.1)octane and 6-(β-chloroethyl)-7-chloromethyl-1-azabicyclo (3.2.1)octane.

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SYNTHESIS OF γ-AMINO KETONES

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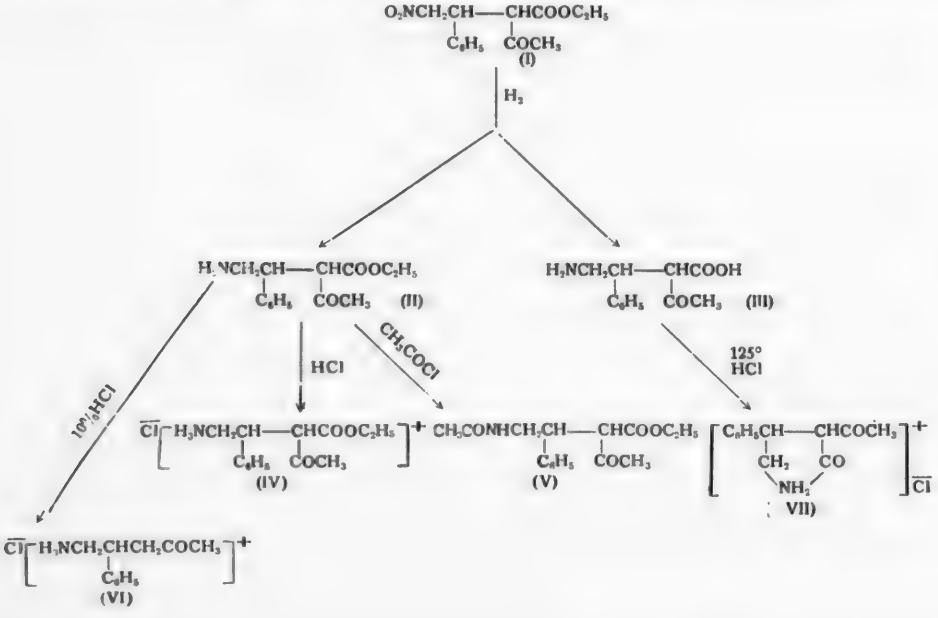
The successful reaction of nitroolefins with acetoacetic ester [1–3] made it possible to use this reaction for developing a new method of obtaining γ-amino ketones, compounds that have been left practically unstudied due to lack of accessible methods for their synthesis, and possessing interest due to the possibility of their heterocyclization to various types of pyrroline derivatives.

It also seemed of interest to establish the relationship between the structure of unsaturated nitro compounds and their ability to condense with acetoacetic ester.

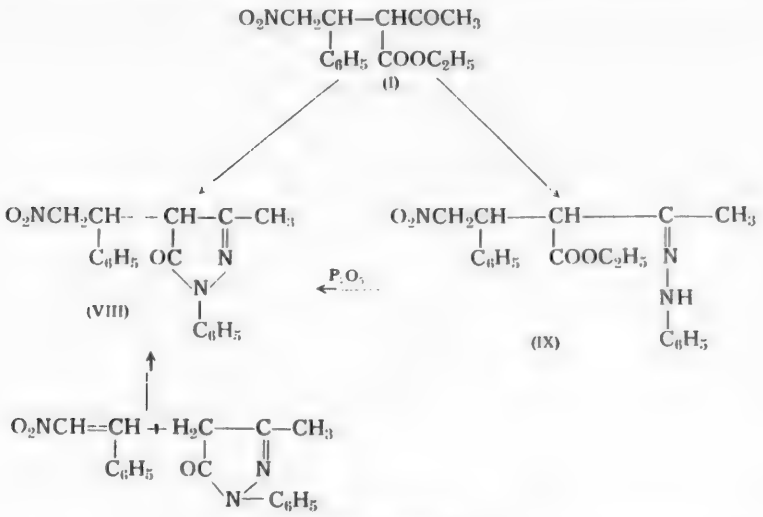
The reaction of nitrostyrene with acetoacetic ester, catalyzed by either triethylamine or pyridine, led to the formation of the ethyl ester of 2-acetyl-3-phenyl-4-nitrobutyric acid (I) in high yields (98 and 82%, respectively). Depending on the length of reaction, the catalytic reduction of the ester gave two products: when the hydrogenation was for 10 hours only the nitro group was attacked and the reduction product was the ethyl ester of 2-acetyl-3-phenyl-4-aminobutyric acid (II), while hydrogenation for 48 hours was accompanied by saponification of the ester and the formation of 2-acetyl-3-phenyl-4-aminobutyric acid (III).

The amino keto ester (II) was subjected to various chemical transformations: 1) saturation of a benzene solution of the ester with dry hydrogen chloride gave the corresponding hydrochloride (IV); 2) treatment of the ester with acetyl chloride gave the acetyl derivative (V), 3) heating the ester with 10% hydrochloric acid led to achieving the main objective: as the result of ketonic cleavage the γ-amino ketone, 1-amino-2-phenyl--4-pentanone (VI), isolated as the hydrochloride, was obtained in 45% yield.

When heated above its melting point the amino acid (III) readily underwent heterocyclization to the pyrrolidone derivative, which when treated with dry hydrogen chloride gave the hydrochloride of 3-phenyl-4--acetyl-5-pyrrolidone (VII).



Special attention was given to establishing the structure of condensation product (I). In alcohol medium with phenylhydrazine in the presence of hydrochloric acid it formed the phenylmethylpyrazolone derivative (VIII), which proved to be identical with the reaction product of nitrostyrene and phenylmethylpyrazolone; hydrazone (IX), synthesized from (I), when heated in benzene in the presence of phosphorus pentoxide was converted to pyrazolone (VIII). As a result, the structure of the condensation product of nitrostyrene with acetoacetic ester failed to evoke any doubt.



EXPERIMENTAL

Ethyl 2-acetyl-3-phenyl-4-nitrobutyrate (I). A solution of 0.52 g (0.0035 mole) of ω-nitrostyrene and 0.58 g (0.0045 mole) of ethyl acetoacetate in 5 ml of anhydrous benzene was treated with 4 drops of pyridine. The mixture was kept protected from moisture at 15° for 12 hours. Removal of the solvent by evaporation (at room temperature) gave the ethyl ester of α-acetyl-β-phenyl-γ-nitrobutyric acid [2] as white needle crystals with m.p. 76°. Yield 0.8 g (82%).

Ethyl 2-acetyl-3-phenyl-4-aminobutyrate (II). A suspension of 2 g of freshly prepared skeletal nickel catalyst in 20 ml of methyl alcohol was saturated for 1 hour with hydrogen at room temperature and vigorous shaking until absorption was complete. Then a solution of 2 g of ethyl 2-acetyl-3-phenyl-4-nitrobutyrate (I) in 50 ml of methanol was added in a hydrogen stream, and the hydrogenation run at 18–20° with vigorous shaking for 10 hours; the hydrogen consumed was 480 ml (calculated 481.6 ml). The catalyst was separated by filtration and then washed three times on the filter with 25 ml of methanol. The methanol filtrate was diluted with 3 volumes of cold water. In approximately 30 minutes a white crystalline precipitate deposited from solution, which was dried over alkali. Yield 0.8 g (45%).

Successive recrystallization from ether and then benzene gave the ethyl ester of 2-acetyl-3-phenyl-4--aminobutyric acid as white needles with m.p. 114°; soluble in methanol and ethanol, acetone, benzene, ether, in dilute alkali and mineral acid solutions, and when heated in 10% soda solution; insoluble in water.

Found %: C 67.55, 67.15; H 7.53, 7.42; N 5.95, 5.84. M 267, 221. $C_{14}H_{19}O_3N$. Calculated %: C 67.42; H 7.68; N 5.62. M 249.2.

2-Acetyl-3-phenyl-4-aminobutyric acid (III). To a suspension of 3.2 g of skeletal nickel catalyst, previously saturated with hydrogen, was added a solution of 2 g of (I) in 50 ml of methyl alcohol in a hydrogen stream, and the hydrogenation run at 18-20° with vigorous shaking for 48 hours; the hydrogen consumed was 500 ml (calculated 481.6 ml). Then the reaction mass was worked up in the same manner as in the preceding case. Yield 0.8 g (50.6%). (III) was obtained as white needles with m.p. 125° (from benzene). Its mixture with (II) had m.p. 105°. 2-Acetyl-3-phenyl-4-aminobutyric acid is soluble in methanol and ethanol, acetone, ether, in dilute alkalies, and when heated in 10% soda solution and in mineral acids.

Found %: C 64.92, 64.93; H 7.08, 6.88; N 6.16, 6.06. M 216, 213. $C_{12}H_{15}O_3N$. Calculated %: C 65.12; H 6.83; N 6.33. M 221.1.

Ethyl 2-acetyl-3-phenyl-4-aminobutyrate hydrochloride (IV). Dry hydrogen chloride was bubbled for 10 minutes into a solution of 0.1 g of the amino ester (II) in 10 ml of benzene, and here product (IV) deposited as a white crystalline precipitate with m.p. 171°, exceedingly soluble in water. Yield 0.11 g (99%). Treatment of a water solution of the salt with 10% soda solution resulted in the separation of the original amino ester (II).

Ethyl-2-acetyl-3-phenyl-4-acetamidobutyrate (V). A solution of 1.25 g (0.005 mole) of amino ester (II) in 25 ml of benzene was treated with 3 g (0.042 mole) of acetyl chloride; in a short time the hydrochloride deposited copiously as a precipitate. The suspension was boiled without the admittance of moisture for 4 hours, and here the precipitate went into solution in 30 minutes. Evaporation of the solution left a tarry residue, which when rubbed with ether was converted into white fluffy crystals. Yield 0.9 g (61.5%). The acetyl derivative (V) with m.p. 205° (from alcohol-ether mixture) is readily soluble in the cold in methanol and ethanol, acetone, benzene and dioxan; difficultly soluble in ether and n-hexane; insoluble in water.

Found %: C 66.16, 66.11; H 6.87, 7.12; N 5.13, 4.79. M 290, 312. $C_{16}H_{21}O_4N$. Calculated %: C 65.93; H 7.26; N 4.81. M 291.2.

1-Amino-2-phenyl-4-pentanone hydrochloride (VI). A solution of 0.5 g of amino ester (II) in 25 ml of 10% hydrochloric acid was refluxed for 4 hours, the small amount of tar obtained here separated by filtration, and the slightly colored hydrochloric acid solution evaporated to dryness. The residual tar after rubbing with acetone was converted to a slightly colored crystalline product, which was washed on the filter with small portions of ether. Yield 0.4 g (95%). Product (IV) with m.p. 165° is readily soluble in cold water, methanol and ethanol.

Its mixture with the amino ester hydrochloride (IV) gave a melting point depression (135°).

Found %: N 6.54, 6.33. M 207, 208 (potentiometric titration). $C_{11}H_{16}ONCl$. Calculated %: N 6.55. M 213.6.

3-Phenyl-4-acetyl-5-pyrrolidone hydrochloride (VII). Amino ester (III) (0.2 g) was heated to the melting point (125°) and then kept at this temperature for 5 minutes. The brown tar obtained here was dissolved in 5 ml of benzene and the solution saturated with dry hydrogen chloride until it showed acid. The tar, isolated after evaporation of the benzene, was converted by rubbing with acetone to a colored crystalline product, which was filtered and washed with small portions of ether. Yield 0.10 g (50%). M.p. 168°. The compound is readily soluble in water; its mixture with amino ketone hydrochloride (VI) gives a melting point depression.

1-Phenyl-3-methyl-4-(α-phenyl-β-nitroethyl)-5-pyrazolone (VIII). A hot solution of 1 g (0.0036 mole) of nitro ester (I) in 20 ml of alcohol was treated with 0.4 g (0.0037 mole) of phenylhydrazine and 3 drops of concentrated hydrochloric acid. The mixture was brought to a boil. After standing at room temperature for a week the solution deposited coarse transparent crystals as long rods with m.p. 85° (from ethanol). Yield 0.6 g (69%).

Reaction of ω-nitrostyrene with 1-phenyl-3-methyl-5-pyrazolone. Synthesis of pyrazolone derivative (VIII). a) A solution of the sodio derivative of 1-phenyl-3-methyl-5-pyrazolone (obtained by the addition of 0.5 g of sodium metal to a solution of 1.74 g of phenylmethylpyrazolone in 30 ml of anhydrous methanol) was treated at 10–15° with a solution of 1.49 g of nitrostyrene in 20 ml of anhydrous methanol. The mixture was heated without the admittance of moisture for 2 hours at 50–55°; the red solution after cooling was neutralized with glacial acetic acid, and then was saturated at 0–5° with dry hydrogen chloride until it showed acid. A finely crystalline precipitate deposited when the pale yellow solution was poured into a mixture of ice and soda, which after 2 hours was filtered and washed with cold water. Yield 3 g (92.8%). Product (VIII) was obtained slightly colored, has a finely crystalline structure, and is soluble in methanol and ethanol, acetone, ether, and in dilute alkali and hydrochloric acid solutions (when heated). M.p. 85° (ethanol).

b) A mixture of 1.49 g of nitrostyrene in 20 ml of anhydrous methanol and 1.74 g of phenylmethylpyrazolone in 30 ml of anhydrous methanol was treated with 6 drops of Rodionov catalyst (alcohol solution of trimethylphenylammonium hydroxide). The mixture was kept at 15–20° for 12 hours without the admittance of moisture. Removal of the solvent by evaporation left coarse transparent crystals with m.p. 85° (ethanol).

Its mixture with product (VIII) did not depress the melting point. Yield 3 g (92.8%).

Found %: C 66.79, 67.13; H 5.60, 5.45; N 12.92, 12.76. M 316, 305. $C_{18}H_{17}O_3N_3$. Calculated %: C 66.83; H 5.30; N 13.02. M 323.2.

Ethyl 2-acetyl-3-phenyl-4-nitrobutyrate phenylhydrazone (IX). A hot solution of 1 g (0.0036 mole) of nitro ester (I) in 20 ml of alcohol was treated with 0.4 g (0.0037 mole) of phenylhydrazine. After standing for a week at room temperature the separated tarry substance was pressed on porous plate. Yield 0.8 g (60.6%). Phenylhydrazone (IX) was obtained as white crystals with m.p. 108° (ethanol); readily soluble in benzene, acetone and ether, and less soluble in methanol and ethanol. It gradually turns to a tar on long standing.

Found %: C 64.91, 64.98; H 6.30, 6.02; N 11.33, 11.42. M 364, 383. $C_{20}H_{23}O_4N_3$. Calculated %: C 65.04; H 6.27; N 11.38. M 369.2.

Conversion of phenylhydrazone (IX) to pyrazolone derivative (VIII). A solution of 0.3 g of hydrazone (IX) in 25 ml of anhydrous benzene was treated with 0.10 g of phosphorus pentoxide and the mixture refluxed for 4 hours without admitting moisture. Then the cold benzene was decanted, while the tar remaining on the bottom of the flask was treated with warm water. As the water cooled, the tar when rubbed with a rod gradually became crystalline. The substance was separated on a filter, and then washed with several portions of water. Yield 0.15 g (58%). After recrystallization from alcohol the finely crystalline product had m.p. 85°. Its mixed melting point with product (VIII), obtained from compound (I), was not depressed.

SUMMARY

A new and accessible method for the synthesis of γ-amino ketones was proposed.

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SYNTHESIS OF VINYL MONOMERS

III. SYNTHESIS OF COMPOUNDS WITH A CARBONYL GROUP

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One of the convenient methods for the synthesis of aryl alkenyl ketones, having general significance, is the Mannich reaction.

Statements have been made that in a number of cases the ease with which the Mannich reaction proceeds is dependent on the nature of the free base used. Thus, Levvy and Nisbet [1] state that 2-acetylfuran and formaldehyde react with the salts of dimethylamine and dipropylamine, but do not react with the salt of diethylamine. Mannich and Heilner [2] described the preparation of phenyl vinyl ketone using dimethylamine hydrochloride. Young and Roberts [3] used diethylamine hydrochloride in the preparation of the same ketone. We used both of the indicated salts in the synthesis of phenyl vinyl ketone, and became convinced that the reaction proceeds much slower and the yield of dialkylaminopropiophenone hydrochloride is much lower when diethylamine hydrochloride is used than when dimethylamine hydrochloride is used (63 and 73.5%, respectively). Phenyl isopropenyl ketone was synthesized from dimethylaminomethylpropiophenone, the latter having been prepared by the method described by Knott [4]. It proved that propiophenone and paraformaldehyde do not react with diethylamine hydrochloride.

The Mannich method was also used by us to obtain the previously unknown 2,5-dichlorophenyl vinyl ketone. 2,5-Dichloroacetophenone and paraform react with diethylamine hydrochloride only to a very slight degree. The reaction with dimethylamine hydrochloride proceeds more easily; the obtained dimethylamino--2,5-dichloropropiophenone hydrochloride had m.p. 162°. 2,5-Dichlorophenyl vinyl ketone was obtained as a slightly green liquid with b.p. 106–107° (5 mm). The ketone polymerizes with extreme ease when distilled, even when distilled in vacuo in the presence of inhibitor. In connection with the greater tendency shown by 2,5-dichlorophenyl vinyl ketone to polymerize when compared with the unsubstituted phenyl vinyl ketone, it is interesting to mention that 2,5-dichlorostyrene also polymerizes more easily than does unsubstituted styrene itself [5]. In the literature relating to the simpler unsaturated aldehydes acrolein and methacrolein, only patent data exist on the preparation of the oximes of these aldehydes. The method described for the preparation of acrolein oxime is based on the conventional reaction with hydroxylamine [6]. Methacrolein oxime was obtained from the addition product of nitrosyl chloride to isobutylene [7,8]. We synthesized the latter oxime by reacting methacrolein with hydroxylamine. The reaction proceeds with ease and gives the oxime in 65% yield. In contrast to acrolein oxime, for which polymers are described [9], methacrolein oxime under block polymerization conditions, when either benzoyl peroxide or azobisisobutyronitrile is used as polymerization initiator, does not polymerize.

EXPERIMENTAL

Phenyl vinyl ketone was obtained by the method of [2]. The yield of dimethylaminopropiophenone hydrochloride was 73.5%.

Found %: Cl 16.29. $C_{11}H_{16}ONCl$. Calculated %: Cl 16.64.

When the synthesis was run using diethylamine hydrochloride the diethylaminopropiophenone hydrochloride was obtained crystalline only after the reaction mixture had been evaporated to small volume. In this case the yield of the ketone was 63%.

The pyrolysis of dimethylaminopropiophenone hydrochloride was run in a vacuum (at a pressure of 5 mm). A mixture of 30 g of the hydrochloride and 0.5 g of hydroquinone was heated at 200–210°. The volatile pyrolysis products were collected in the range 70–120°, dried over sodium sulfate, and fractionally distilled several times in vacuo (with the addition of hydroquinone). We obtained 8.3 g (45%) of phenyl vinyl ketone.

B.p. 74–76° (4 mm), d^{20}_4 1.0387, $n^{20}D$ 1.5550.

From [3]: B.p. 72–73° (3 mm).

Phenyl isopropenyl ketone was obtained from dimethylaminomethylpropiophenone hydrochloride, the latter having been prepared by the Knott method [4]. This hydrochloride was pyrolyzed in the same manner as in the preceding synthesis. Yield of phenyl isopropenyl ketone 48.7%, based on the salt of the Mannich base, or 33.6%, based on starting propiophenone.

B.p. 83.5–85° (7 mm), d^{20}_4 1.0139, $n^{20}D$ 1.5373.

Found %: C 82.01; H 5.9. $C_{10}H_{10}O$. Calculated %: C 82.19; H 6.85.

When an attempt was made to react diethylamine with propiophenone and paraformaldehyde the diethylamine hydrochloride was recovered practically unchanged from the reaction mixture. The starting propiophenone was prepared by the Read method [10].

2,5-Dichlorophenyl vinyl ketone. A mixture of 25 g of 2,5-dichloroacetophenone, 4.4 g of paraformaldehyde, 12.6 g of dimethylamine hydrochloride, 50 ml of anhydrous alcohol and 0.2 ml of concentrated hydrochloric acid was heated with stirring for 6 hours on the boiling water bath. Then the mixture was poured into a dish and allowed to stand overnight in a desiccator. The obtained crystals were filtered and washed with dry ether. We obtained 16 g of dimethylamino-2,5-dichloropropiophenone hydrochloride.

After recrystallization from anhydrous alcohol, m.p. 162°.

Found %: Cl 12.59; N 4.77. $C_{11}H_{14}ONCl_3$. Calculated %: Cl 12.55; N 4.95.

The hydrochloride was pyrolyzed in the same manner as in the preceding syntheses. The yield of 2,5-dichlorophenyl vinyl ketone, obtained as a slightly green liquid, was 17.2%, based on starting 2,5-dichloroacetophenone.

B.p. 106–107° (5 mm), d^{20}_4 1.320, $n^{20}D$ 1.5698, MR 49.90; calculated 49.44.

Found %: C 53.85, 54.10; H 2.99, 3.30; Cl 37.43, 37.32. $C_9H_6OCl_2$. Calculated %: C 53.75; H 2.99; Cl 35.36.

When vacuum-distilled the ketone showed substantial polymerization even in the presence of an inhibitor. The starting 2,5-dichloroacetophenone was prepared [11] by heating a mixture of 50 g of p-dichlorobenzene, 50 g of acetyl chloride and 100 g of aluminum chloride on the boiling water bath for 5 hours. At the end of reaction the mixture was poured on ice, 30 ml of concentrated hydrochloric acid was added, and the product was steam-distilled. The distillate was extracted with ether. Fractionation in vacuo gave a fraction with b.p. 109–113° (7 mm). Yield of 2,5-dichloroacetophenone 50%.

Methacrolein oxime. A solution of 11 g of hydroxylamine hydrochloride in 30 ml of water, containing 0.5 g of N-phenyl-β-naphthylamine (antioxidant), was gradually treated with 7.5 g of sodium carbonate. When all of the sodium carbonate had dissolved the mixture was cooled to -10°, and then 10 g of methacrolein was added dropwise to it in 30–40 minutes with stirring. After stirring for another 15 minutes at -10° the obtained organic layer was separated from the bottom water layer. The water layer was extracted twice with ether, and the ether extract was added to the upper layer. The ether solution was then washed with water and dried over calcium chloride. The residue obtained after distilling off the ether was vacuum-distilled in the presence of N-phenyl-β-naphthylamine. After two distillations we obtained 8 g (65%) of methacrolein oxime.

B.p. 48.5° (12 mm), d^{20}_4 0.9487, $n^{20}D$ 1.4852, MR 25.69; calculated 24.21.

Literature data: B.p. 51–53° (15 mm); 45–46° (6 mm); 143–148° (760 mm).

According to [7]: $n^{19.5}D$ 1.4430; [8]: $n^{20}D$ 1.4789.

Found %: C 58.20, 57.98; H 8.46, 8.38; N 16.54, 16.70. C_4H_7ON. Calculated %: C 56.43; H 8.31; N 16.47.

The methacrolein used for the synthesis was prepared by the oxidation of methallyl alcohol, using the method of Church and Lynn [12].

SUMMARY

1. The Mannich method was used to synthesize phenyl vinyl ketone, phenyl isopropenyl ketone and the previously unknown 2,5-dichlorophenyl vinyl ketone. It was established that propiophenone and paraformaldehyde react with dimethylamine hydrochloride in the Mannich sense, but do not react with diethylamine hydrochloride.

2. Methacrolein oxime was synthesized by the reaction of methacrolein with hydroxylamine.

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SYNTHESIS OF DIUREINES OF SOME NITROPHENANTHRENEQUINONES

D. F. Kutepov, A. A. Potashnik and D. N. Khokhlov

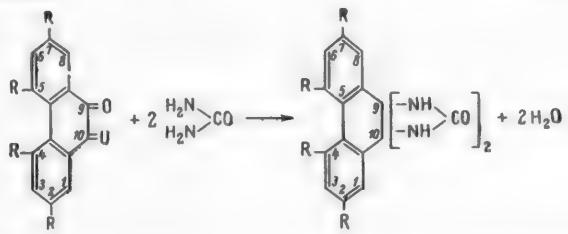
Phenanthrenequinonediureine (I) was obtained by Grimaldi [1] by the fusion of phenanthrenequinone with a large excess of urea at 250°. The author indicates that the isolation and purification of (I) present great difficulties due to the insolubility of both (I) and the other transformation products of urea, found in large amounts in the melt.

It is known that the diureines of α-diketones are easily obtained by reacting urea with the diketone in either aqueous or alcoholic medium in the presence of mineral acid [2,3].

Considering the similarity in the chemical properties of α-diketones and o-quinones, we extended the indicated reaction to phenanthrenequinone and its nitro derivatives. The diureines are formed using an acidulated boiling aliphatic alcohol as the medium. The reaction rate depends on the boiling point of the alcohol. If (I) is formed in small amount under the conditions of prolonged boiling in ethyl alcohol as the medium, then in n-butyl alcohol medium the reaction is ended in 3 hours and the yield of product is 85.5%.

Using similar conditions we obtained the previously unknown diureines in 70.3–88.5% yield: 2-nitrophenanthrenequinonediureine (II), 4-nitrophenanthrenequinonediureine (III), 2,7-dinitrophenanthrenequinonediureine (IV) and 4,5-dinitrophenanthrenequinonediureine (V).

According to the literature [2,3], the diureines of α-diketones are compounds with two imidazole rings; apparently, the diureines (I–V), obtained by us from a quinone and urea by the scheme given below, also contain two imidazole rings in the molecule



where R = H or NO_2.

It was established that the position and number of nitro groups in the phenanthrenequinone molecule exert great influence on the reaction rate of the latter with urea. A nitro group in position 4 and two nitro groups in the 4,5 positions facilitate condensation of the quinone with urea, whereas a nitro group in position 2 and two nitro groups in the 2, 7 positions greatly hinder this reaction when compared with the reaction of unsubstituted phenanthrenequinone with urea.

The reaction rate of the quinones investigated by us with urea decreases in the order: 4-nitrophenanthrenequinone, 4,5-dinitrophenanthrenequinone, unsubstituted phenanthrenequinone, 2-nitrophenanthrenequinone, and 2,7-dinitrophenanthrenequinone. Thus, for example, in boiling ethyl alcohol the reaction for the formation of (III) and (V) is ended in 1.5–2 hours, (I) is formed in small amount after heating for many hours, while (II) and (IV) are not obtained under these conditions. In boiling n-butyl alcohol (b.p. 117°), (III) and (V) are obtained in good yields when the heating is for 1 hour, (I) is obtained in good yield when the heating is for 3 hours, while

(II) and (IV) are formed only in small yields when the heating is for many hours; however, the last two diureines were obtained in good yields when the reaction was run in isoamyl alcohol medium (b.p. 132°).

The alcohol was used in such amount that the quinone went into solution on heating. The reaction can also be run successfully with a smaller amount of the alcohol (here a part of the quinone remains undissolved), but in this case the reaction mixture has to be heated for a much longer time.

To acidulate the medium we used concentrated sulfuric acid in an amount of about 1 ml per 100 ml of solution. Increasing the amount of acid 2–3 times was without appreciable effect on the reaction rate or the yield of diureine. However, a greater acidulation of the medium leads to the formation of tarry substances.

All of the diureines obtained by us are white or slightly colored amorphous powders, insoluble in water and in organic solvents. They do not have melting points, and decompose when heated in a capillary above 300°.

EXPERIMENTAL

Phenanthrenequinonediureine (I). A mixture of 10 g of phenanthrenequinone and 8 g of urea was dissolved in 200 ml of boiling n-butyl alcohol. Then 2 ml of sulfuric acid was added in drops and with stirring to the solution, and the whole boiled under reflux for 3 hours. The deposited (I) was filtered hot, washed with hot ethyl alcohol, then with hot water, and dried. Yield 12.0 g (85.5%). The compound was obtained as a pale orange amorphous substance. M.p. 336–339°.

Found %: C 65.61, 65.25; H 4.52, 4.50; N 18.81, 18.70. $C_{16}H_{12}O_2N_4$. Calculated %: C 65.74; H 4.14; N 19.17.

According to the literature this amorphous powder does not have a melting point. It decomposes when heated strongly, and is insoluble in the common solvents [1].

2-Nitrophenanthrenequinonediureine (II). A mixture of 7.5 g of 2-nitrophenanthrenequinone and 7.5 g of urea was dissolved in 1 liter of isoamyl alcohol (b.p. 132°) with heating, then 10 ml of sulfuric acid was added, and the whole boiled under reflux for 5 hours. (II) was filtered hot, washed with hot glacial acetic acid, then with hot water, and dried. Yield 7.0 g (70.0%); pale yellow powder. M.p. 303–306° (decompn.).

Found %: C 56.44, 56.50; H 3.14, 3.45; N 19.87, 19.66. $C_{16}H_{11}O_4N_5$. Calculated %: C 56.96; H 3.26; N 20.77.

4-Nitrophenanthrenequinonediureine (III) was obtained by the same method used to obtain (I), but here the boiling was for 1 hour. From 5 g of 4-nitrophenanthrenequinone and 5 g of urea we obtained 5.9 g (88.5%) of a white powder. M.p. 310–315° (decompn.).

Found %: C 56.93, 56.60; H 2.70, 2.40; N 20.63, 20.46. $C_{16}H_{11}O_4N_5$. Calculated %: C 56.96; H 3.26; N 20.77.

2,7-Dintrophenanthrenequinonediureine (IV) was obtained by the same method used to obtain (II), but here the heating was for 10 hours. From 1 g of 2,7-dinitrophenanthrenequinone and 1 g of urea in 100 ml of isoamyl alcohol we obtained 0.9 g (70.3%) of a pale pink powder. M.p. 342–345° (decompn.).

Found %: C 50.33, 50.42; H 2.90, 2.94; N 20.77, 20.69. $C_{16}H_{10}O_6N_6$. Calculated %: C 50.26; H 2.64; N 21.99.

4,5-Dinitrophenanthrenequinonediureine (V) was obtained in the same manner as (III). From 2 g of 4,5-dinitrophenanthrenequinone and 2 g of urea in 100 ml of n-butyl alcohol we obtained 2.2 g (86.0%) of a white powder. M.p. 305–308° (decompn.).

Found %: C 51.13, 50.87; H 2.70, 2.65; N 22.12, 21.74. $C_{16}H_{10}O_6N_6$. Calculated %: C 50.26; H 2.64; N 21.99.

SUMMARY

1. A practical and convenient method was developed for the synthesis of the diureines of phenanthrenequinone and its nitro derivatives in 70.3–88.5% yield.

2. The previously unknown 2-nitro-, 4-nitro-, 2,7-dinitro- and 4,5-dinitrophenanthrenequinonediureines were synthesized.

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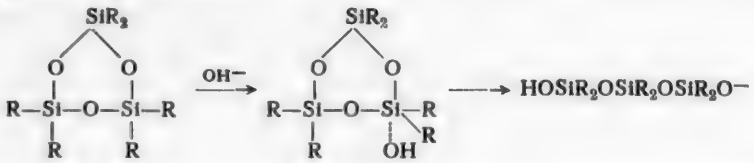
CATALYTIC POLYMERIZATION OF POLYPHENYL- AND POLY(DIMETHYLPHENYL)SILOXANES

K. Andrianov, S. Dzhenchel'skaia and Iu. Petrashko

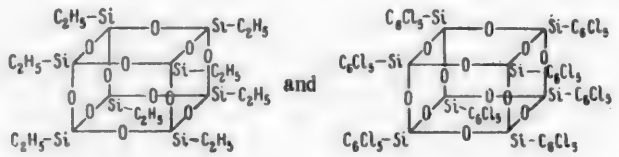
Polyorganosiloxanes are obtained by the hydrolysis of alkyl(aryl)halosilanes or alkyl(aryl)alkoxysilanes with subsequent condensation of the hydrolysis products to polyorganosiloxanes. During hydrolysis, reactions occur that lead to the formation of either linear or cyclic polymers. The cyclic polymers are obtained in the best yield in acid medium, when the hydrolysis is run in an excess of water.

The hydrolysis of bifunctional monomers (dimethyldichlorosilane, phenylmethyldichlorosilane) led to obtaining low-molecular cyclic products—trimers, tetramers and higher cycles [1]. In the presence of catalysts (sulfuric acid, antimony pentachloride [2], potassium hydroxide [3], ferric chloride [4]), the cyclic compounds obtained in the hydrolysis of the bifunctional compounds are capable of rearrangement with rupture of the cycles. Thus, the polymerization of the cycles obtained from dimethyldichlorosilane, under the influence of caustic alkalies, proceeds by the scheme

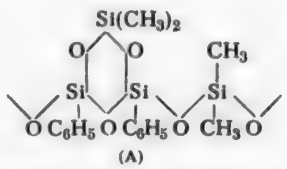


Recently it was established that the hydrolysis of trifunctional compounds in acid medium also results in the formation of cyclic polymeric compounds.

The hydrolysis of ethyltriethoxysilane [5] and pentachlorophenyltrichlorosilane [6] gave crystalline cyclic polymers with the structure



The cohydrolysis of phenyltrichlorosilane with dimethyldichlorosilane in acid medium also gives cyclic polymers of a mixed type (A).



(A)

Due to the importance of the conversion of tri- and bifunctional alkyl(aryl)halosilanes to polymers, an attempt was made in the present work to study the alkaline catalytic polymerization of the cyclic compounds

obtained in the hydrolysis of phenyltrichlorosilane, and also of the cohydrolysis products of phenyltrichlorosilane with dimethyldichlorosilane.

Comparative experiments on the polymerization of octamethylcyclotetrasiloxane and poly(dimethylphenyl)cyclosiloxane with sodium hydroxide revealed that a noticeable change in the viscosity of the product was not observed when octamethylcyclotetrasiloxane was treated with 1% NaOH at 20° for a long time, but that the viscosity rose rapidly when the reaction temperature was raised to 120–130°. However, for the cohydrolysis products of phenyltrichlorosilane with dimethyldichlorosilane (polydimethylphenylcyclosiloxane), treatment with 1% NaOH at 20° causes the viscosity to increase rapidly and the polymer to change to a gel within 35–40 minutes.

To study the influence of the amount of NaOH on the rates of viscosity increase and gel formation at 20° we used a 58% toluene solution of the cohydrolysis products of phenyltrichlorosilane with dimethyldichlorosilane. The experimental data, shown in Fig. 1, reveal that the time required for transition of the polymer into

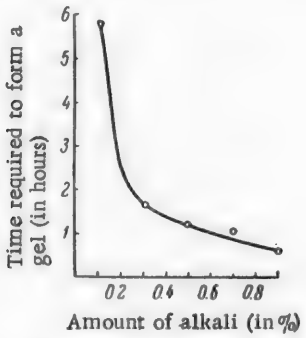


Fig. 1. Effect of amount of alkali on rate of gel formation.

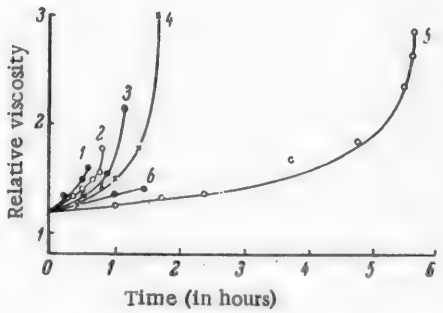


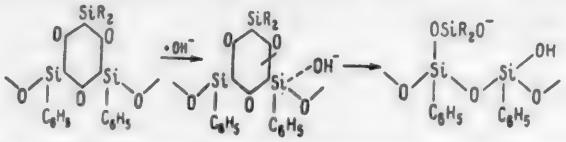
Fig. 2. Relationship between the viscosity and the time of polymerization with various amounts of alkali. Amount of alkali (in %): 1) 0.9, 2) 0.7, 3) 0.5, 4) 0.3, 5) 0.1, 6) 0.9 (40°).

a gel is inversely proportional to the amount of added sodium hydroxide. The relationship between the viscosity and the time of polymerization in the presence of various amounts of catalyst is shown in Fig. 2. The rate of rise in the viscosity of the polymer increases with increase in the amount of catalyst. In addition, the greater the amount of alkali taken, the lower is the viscosity of the polymer at which it changes into a gel. Thus, with 0.9% NaOH the polymer changes into a gel within 30 minutes and a 10% solution of the polymer in toluene has a relative viscosity of 1.5 at the point of transition into a gel, whereas with 0.1% alkali the relative viscosity of the polymer at the transition point is greater than 2.8, and it takes 5.7 hours for the polymer to change to a gel. Curve 6 in Fig. 2 shows the increase in the viscosity of the cyclic polymer obtained from phenyltrichlorosilane when treated with 0.9% sodium hydroxide at 40°. It is interesting to mention that for the given polyphenylsiloxane at 20° and the indicated amount of alkali an increase in the viscosity is not observed even after some 20–30 hours. As can be seen from Fig. 2, for the given polyphenylsiloxane even at 40° the viscosity increases with time more slowly than in the case of the poly(dimethylphenyl)siloxane at 20° and 0.3% sodium hydroxide.

In contrast to octamethylcyclotetrasiloxane, the cyclic polymers obtained by the cohydrolysis of phenyltrichlorosilane with dimethyldichlorosilane, show polymerization at 20° even in the presence of 0.1% NaOH, and the polymers, obtained from phenyltrichlorosilane, in the presence of 0.9% NaOH at 40°.

To determine the influence of concentration on the conversion rates of the poly(dimethylphenyl)siloxanes we ran some experiments with solutions of the polymer in toluene at a concentration of 40, 52.3, 58 and 71%, in the presence of 0.3% NaOH. As can be seen from Fig. 3, the rate of increase in the viscosity decreases and the time required for transition of the polymer into a gel increases as the concentration of the polymer is reduced.

It is possible to assume that the first stage in the reaction with alkali is the formation of an intermediate activated complex due to reaction of the donor hydroxyl group of the sodium hydroxide with the silicon atom.



Such an activated complex causes rupture of the weakened silicon–oxygen bond and forms an ion.

The presence of steric hindrance in the cycle, weakening the strength of the bonds in the molecules, should facilitate progress of this reaction. The formed ion attacks a second cyclic molecule, rupturing the Si–O bond, and adds to it. In this manner, both the molecular chain and its branching increase. The final moment of reaction should be closure of the high-molecular molecule with the formation of larger cycles. If a rupturing factor is present in the reaction sphere then it is possible for reaction to be terminated by the formation of branched and three-dimensional polymers.

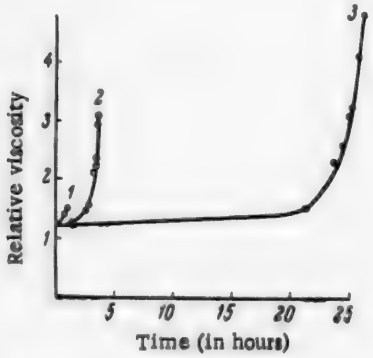


Fig. 3. Effect of the concentration of solutions of the polymer in toluene on the rate of increase in the viscosity. Concentration of solutions (in %): 1) 71, 2) 52.3, 3) 40.

The experiments revealed that the cycles, formed in the cohydrolysis of bi- and trifunctional compounds, in particular of dimethyldichlorosilane and phenyltrichlorosilane, when treated with aqueous sodium hydroxide are converted with greater ease than are the cycles obtained from phenyltrichlorosilane and bifunctional monomers, for example, octamethylcyclotrisiloxane. The process for the polymerization of the cyclic products obtained from phenyltrichlorosilane and from phenyltrichlorosilane with dimethyldichlorosilane proceeds with the formation of soluble polymers, and only when a certain viscosity is reached, different for each catalyst concentration used, is a transition of the polymer from a soluble to an insoluble gel-like state observed. The fact that the time required to form a gel is inversely proportional to the amount of added caustic indicates that the more caustic introduced into the reaction, the greater the number of active particles formed per unit of time, and the more rapid is the growth of the molecular chains, and therefore the viscosity.

With reduction in the solution concentration of the polymer the rate of increase in the viscosity decreases and the time required to form a gel increases. This can be explained by stating that the number of cyclic molecules per unit volume of reaction mixture decreases with increase in the dilution, which leads to a reduction in the number of contacts between the cyclic molecules and the growing active centers, as a result of which the reaction rate is lowered.

The greater rate at which the cycles are rebuilt in the case of the poly(dimethylphenyl)siloxanes, when compared to the polyphenylsiloxanes, should be explained as being due to the steric hindrance created by the phenyl groups.

EXPERIMENTAL

Preparation of polyphenylsiloxane. A mixture of 2600 g of water and 634.5 g of toluene was charged into the hydrolyzer, fitted with a water jacket, thermometer and dropping funnel. Then a solution of 634.5 g of phenyltrichlorosilane in 634.5 g of toluene was added to the hydrolyzer with constant stirring. The temperature of the reaction mixture was kept constant at 20°. Then the mixture was stirred for another hour, after which the polymer was separated from the water, washed with water until neutral to Congo, and dried to constant weight. A hard brittle product with m.p. 43–46° was obtained.

Found %: C 55.8; H 3.88; Si 21.7. $(C_6H_5SiO_{1.5})_x$. Calculated %: C 55.8; H 3.86; Si 21.7.

Preparation of poly(dimethylphenyl)siloxane. A mixture of 360 g of water and 180 g of toluene was charged into the hydrolyzer, fitted with cooling jacket, stirrer, thermometer and dropping funnel. Then a mixture of 68 g of dimethyldichlorosilane, 112 g of phenyltrichlorosilane and 180 g of dry toluene was added with constant stirring. The temperature of the mixture was kept constant at 20°. The mixture was stirred for 1 hour, after which the organic layer was separated from the water layer, washed with water until neutral, filtered, and the toluene removed from it by distillation. The obtained product was subjected to elemental analysis.

Found %: C 48.91; H 5.81; Si 29.01. $(C_8H_{11}O_2Si_2)_x$. Calculated %: C 49.23; H 5.64; Si 28.72.

Catalytic polymerization of polyphenylsiloxane. A 59.1% solution of 60 g of polyphenylsiloxane in toluene was placed in a round-bottomed flask fitted with dip tube and stirrer. Then a 39.36% NaOH solution (calculated as 0.9% on the polyphenylsiloxane) was added with vigorous stirring to the polycyclophenylsiloxane solution at 40°. The temperature during reaction was kept at 40°. Samples of the polymer were removed at periodic intervals and their relative viscosity as a 10% solution of the polymer in toluene was determined (by the Ostwald method). The reaction was stopped when a gel had formed. The experiments on the polymerization of the polyphenylsiloxane with 0.5 and 0.8% sodium hydroxide at 20° failed to lead to an increase in the viscosity of the product even after more than 100 hours.

Catalytic polymerization of poly(dimethylphenyl)siloxane. The experiments on the catalytic polymerization of the cohydrolysis products of dimethyldichlorosilane with phenyltrichlorosilane were run at 20°. The concentration of the polymer in toluene was 58.5%. Using the indicated conditions the experiments were run with a variable amount of sodium hydroxide (0.3, 0.5, 0.7 and 0.9% on the weight of polymer).

We also investigated the influence of the polymer concentration in toluene (using 0.3% NaOH) on the rates of gel formation and viscosity increase. The obtained data are shown in Figures 1–3.

SUMMARY

The catalytic polymerization of cyclic polyphenylsiloxanes, poly(dimethylphenyl)siloxanes and octamethylcyclotetrasiloxane was studied. It was established that the polydimethylphenylsiloxanes polymerize with greater ease than the polyphenylsiloxanes; octamethylcyclotetrasiloxane is polymerized when treated with small amounts of sodium hydroxide only on heating.

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SOME DERIVATIVES OF MERCAPTOCAFFEINE AND MERCAPTOTHEOBROMINE

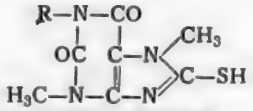
E. G. Berdichevskii, F. Iu. Rachinskii and E. K. Novoselova

The importance of sulfhydryl compounds in physiological processes is a universally studied subject. In this connection the mercapto derivatives of caffeine and theobromine are of especial interest.

Mercaptopurines and mercaptoxanthines were first obtained by E. Fischer [1], and on the basis of his method a patent was issued on the preparation of 8-mercaptocaffeine by the reaction of 8-chlorocaffeine with potassium hydrosulfide [2]. Literature data on the preparation and properties of 8-mercaptotheobromine are lacking. The synthesis of 8-mercaptotheophylline (1,3-dimethyl-2,6-dihydroxy-8-mercaptopurine) by heating the potassium salt of 1,3-dimethyluric acid with hydrogen sulfide at 150° under pressure is described in a patent [3].

A. M. Khaletskii and M. S. Eshman [4], who synthesized the thio analogs of theobromine by reacting the latter with phosphorus trisulfide, prepared 3,7-dimethyl-2,6-dithiopurine and came to the conclusion that of the two desmotropic forms possible for the dithiotheobromine, either the lactam or the lactim, preference should be given to the latter.

We repeated the synthesis of 8-mercaptocaffeine (I) under somewhat different conditions, using as starting reactants 8-bromocaffeine and an alcoholic solution of sodium hydrosulfide. 8-Mercaptotheobromine (II) was obtained in a similar manner.



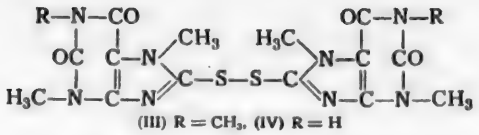
(I) R = CH_3, (II) R = H.

Mercaptocaffeine and mercaptotheobromine are practically insoluble in water, in contrast to their sodium salts (mercaptides). Based on preliminary data, these mercaptides are pharmacologically similar to caffeine and theobromine and can be used in medical practice in place of the soluble pharmacopoeia preparations of caffeine and theobromine. Of practical interest is the replacement of the diurethan of mercaptotheobromine, since the high alkalinity of the diurethan leads to its carbonization and reduces the solubility of the compound in water.

Bearing in mind that mercaptans tend to oxidize, we set out to protect the sulfhydryl group in order to increase the stability of the obtained compounds. We prepared some derivatives of mercaptocaffeine and mercaptotheobromine by replacing the hydrogen of the sulfhydryl group, on the assumption that in the organism it is possible for sulfides and disulfides to be converted into compounds containing the free sulfhydryl group.

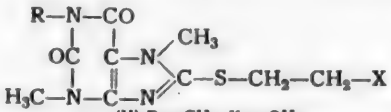
$$R{-}S{-}R + 2H \rightleftarrows R{-}SH + HR$$
$$R{-}S{-}S{-}R + 2H \rightleftarrows 2R{-}SH$$

The careful oxidation of mercaptocaffeine and mercaptotheobromine gave the corresponding disulfides (III) and (IV). Both of the latter compounds are practically insoluble in water, and for this reason are hardly suitable for pharmacological testing.



(III) R = CH_3, (IV) R = H

Reaction of the sodium salts of mercaptocaffeine and mercaptotheobromine with ethylene chlorohydrin gave respectively 1,3,7-trimethyl-2,6-dihydroxy-8-thiopurineethanol (V) and 3,7-dimethyl-2,6-dihydroxy--8-thiopurineethanol (VI), soluble to the extent of 1–4% in water at room temperature.



(V) R = CH_3, X = OH;
(VI) R = H, X = OH;
(VII) R = CH_3, X = NH_2;
(VIII) R = H, X = NH_2.

We also prepared the mercaptoamine derivatives in which the hydrogen of the sulfhydryl group was replaced by either caffeine (VII) or theobromine (VIII). The hydrochlorides of both 1,3,7-trimethyl--2,6-dihydroxy-8-thiopurineethylamine and 3,7-dimethyl-2,6-dihydroxy-8-thiopurineethylamine are readily soluble in water.

EXPERIMENTAL

1,3,7-Trimethyl-2,6-dihydroxy-8-mercaptopurine (I). To a suspension of 10 g of 8-bromocaffeine in 25 ml of anhydrous alcohol with vigorous stirring, in the cold, was added 50 ml of an 8% alcoholic solution of sodium hydrosulfide. The mixture was heated to the boil, and kept here until the odor of hydrogen sulfide disappeared. The precipitate was washed with anhydrous alcohol, dissolved in the minimum amount of water and, after treatment with activated carbon, was acidified with 10% HCl solution until acid to litmus. The obtained precipitate was washed with cold water, then with alcohol, and dried in a vacuum-desiccator. Yield 7.3 g (88%).

Found %: S 15.08, 14.62 (Messinger); N 25.01, 24.91 (Kjeldahl). $C_8H_{10}O_2N_4S$. Calculated %: S 14.16; N 24.78.

(I) was obtained as a white powder, with decomposition point around 250°; it is insoluble in water and organic solvents, and readily soluble in an equivalent amount of alkali with the formation of the mercaptide, which is readily soluble in water.

3,7-Dimethyl-2,6-dihydroxy-8-mercaptopurine (II). To a suspension of 10 g of 8-chlorotheobromine in 25 ml of anhydrous alcohol was added 65 ml of an 8% alcoholic solution of sodium hydrosulfide with vigorous stirring. Further treatment was the same as indicated above. Yield 6.8 g (about 68%).

Found %: S 16.14, 15.64; N 26.35, 26.77. $C_7H_8O_2N_4S$. Calculated %: S 15.09; N 26.41.

(II) was obtained as a microcrystalline powder, with decomposition point around 260°; it is insoluble in water and organic solvents. It forms the water-soluble mercaptide with an equivalent amount of sodium hydroxide.

Dicaffeine disulfide (III). Ten grams of the sodium salt of 8-mercaptocaffeine was dissolved in the minimum amount of water and then treated with the equivalent amount of 0.1 N aqueous iodine solution. The obtained precipitate was washed with water and then dried in a vacuum-desiccator. Yield 7.7 g (about 85%).

Found %: S 13.97, 13.91; N 25.31, 25.00. $C_{16}H_{18}O_4N_8S_2$. Calculated %: S 14.22; N 24.89.

(III) was obtained as a lemon-yellow powder, with decomposition point around 200°; it is insoluble in water, alcohol, ether and benzene; readily soluble in chloroform and in a large excess of aqueous sodium salicylate solution.

Ditheobromine disulfide (IV). Ten grams of the sodium salt of 8-mercaptotheobromine was treated with an equivalent amount of 0.1 N aqueous iodine solution, the same as in the preceding experiment. Yield 7 g (about 82%).

Found %: S 14.87, 14.70; N 26.25, 26.72. $C_{14}H_{14}O_4N_8S_2$. Calculated %: S 15.17; N 26.54.

(IV) was obtained as a yellow powder. Its decomposition point is around 285°; it is insoluble in water and organic solvents.

1,3,7-Trimethyl-2,6-dihydroxy-8-thiopurineethanol (V). A mixture of 10 g of the sodium salt of 8-mercaptocaffeine and 10 g of freshly distilled ethylene chlorohydrin was heated at 120° for 2 hours. The reaction mixture crystallized on cooling. To isolate the product the reaction mass was repeatedly treated with boiling anhydrous alcohol, from which colorless needle crystals deposited on cooling. Some more of the same substance was isolated from the mother liquor. Recrystallization from alcohol gave 8.5 g (about 80%) of crystalline product.

Found %: S 11.71, 11.88; N 21.59, 21.34. $C_{10}H_{14}O_3N_4S$. Calculated %: S 11.85; N 20.74.

(V) was obtained as colorless needle crystals with m.p. 120–122°. The compound is soluble at room temperature in water (up to 1%) and alcohol, and is readily soluble in chloroform.

3,7-Dimethyl-2,6-dihydroxy-8-thiopurineethanol (VI). Ten grams of the sodium salt of 8-mercaptotheobromine was mixed with 20.8 g of freshly distilled ethylene chlorohydrin; further treatment was the same as in the preceding experiment. Yield 8 g (about 73%).

Found %: S 11.95, 11.84; N 21.79, 21.81. $C_9H_{12}O_3N_4S$. Calculated %: S 12.50; N 21.87.

(VI) was obtained as a microcrystalline powder with m.p. 216–218°. It is soluble in water at room temperature (up to 1%); it is practically insoluble in organic solvents.

Hydrochloride of 1,3,7-trimethyl-2,6-dihydroxy-8-thiopurineethylamine (VII). Ten grams of the sodium salt of 8-mercaptocaffeine was added to 550 ml of an alcohol solution of 3.2 g of β-chloroethylamine, obtained from the corresponding hydrochloride. The mixture was heated with constant stirring on the boiling water bath for 5 hours, and then was immediately filtered. HCl gas was passed into the extremely cold filtrate. The resulting hydrochloride precipitate was filtered, washed with anhydrous alcohol, and dried in a vacuum-desiccator. Yield 10 g (about 81%).

Found %: S 9.96, 9.86; N 22.75, 22.74. $C_{10}H_{15}O_2N_5S \cdot HCl$. Calculated %: S 10.48; N 22.91.

(VII) was obtained as a fine white powder, with decomposition point around 249°. It is readily soluble in water at room temperature and in warm alcohol.

Hydrochloride of 3,7-dimethyl-2,6-dihydroxy-8-thiopurineethylamine (VIII). Ten grams of the sodium salt of 8-mercaptotheobromine was added to 320 ml of an alcohol solution of 3.4 g of β-chloroethylamine, obtained from the corresponding hydrochloride; further treatment was the same as in the preceding experiment. Yield 4 g (about 32%).

Found %: S 11.06, 11.41; N 23.13, 23.72. $C_9H_{13}O_2N_5S \cdot HCl$. Calculated %: S 10.98; N 24.01.

(VIII) was obtained as a white powder that sublimed at about 240° (with decompn.). It is readily soluble in water at room temperature, and is insoluble in organic solvents.

SUMMARY

Eight mercaptopurine derivatives were synthesized, of which six were obtained for the first time. Based on preliminary data, the pharmacological properties of the obtained compounds lie close to those of caffeine and theobromine.

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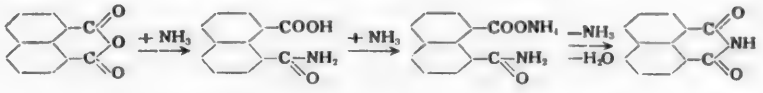
* Original Russian pagination. See C. B. Translation.

SYNTHESIS OF NAPHTHALIMIDE AND ITS DERIVATIVES

A. P. Karishin and D. M. Kustol

Incorrect conditions are given in the literature for the transformation of naphthalic anhydride and its derivatives to the corresponding imides. Some authors indicate that to obtain naphthalimide it is necessary to boil naphthalic anhydride for a long time (from 2 to 8 hours) with either aqueous or alcoholic ammonia solution [1–5], or to heat the mixture in an autoclave for 1–2 hours [6]. Methods are also described for the preparation of naphthalimide in which salts of naphthalic acid are heated with ammonium salts for a long time [7,8]. Similar methods were used to obtain 4-chloronaphthalimide, 4-bromonaphthalimide [9], 4-nitronaphthalimide [10], 4,5-dibromonaphthalimide and 4-bromo-5-chloronaphthalimide [11].

We established that naphthalic anhydride and its monohalo and mononitro derivatives are very easily converted to the corresponding imides when heated with 15–16% aqueous ammonia solution at 60–90° for 25–30 minutes. The yield of the corresponding imides reaches 98%. As our investigations show, the conversion of naphthalic anhydride under these conditions proceeds mainly through the ammonium salt of the monoamide of naphthalic acid, according to the following scheme

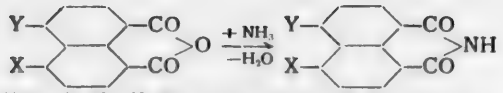


The formation of the ammonium salt of the naphthalic acid monoamide proceeds vigorously even at 50–60°. This salt is readily soluble in water, but is extremely unstable, and when the water solution is boiled it is almost completely (97%) converted to naphthalimide. Acidification of a water solution of the ammonium salt with hydrochloric acid gives the monoamide of naphthalic acid as a precipitate, which when boiled with water or on drying is 96% converted to naphthalic anhydride and 4% to naphthalimide.

The potassium salt of the naphthalic acid monoamide was isolated by us in the free state. This supports the statements made above regarding the existence in solution of the ammonium salt of the naphthalic acid monoamide as an intermediate product in the process for the formation of naphthalimide.

If naphthalic acid is taken to obtain naphthalimide, then its reaction with aqueous ammonia gives the diammonium salt, which when boiled in solution for 6 hours is converted to naphthalimide only to the extent of 70%. From this it follows that in order to obtain good yields of naphthalimide it is necessary to use naphthalic anhydride free of naphthalic acid as impurity, and also to use moderate heating (to avoid rapid loss of ammonia). To accomplish this we used naphthalic anhydride that had been recrystallized from boiling nitrobenzene, or else had been dried at 140–150° for 3–4 hours. Under the indicated conditions, anhydride that had been previously dried at 105–110° for 10 hours gives the imide in a yield not exceeding 84%. The reactions with the monosubstituted naphthalic anhydrides proceed in a similar manner.

The anhydrides of the dihalonaphthalic acids are converted with much greater difficulty to the corresponding imides. To obtain 4,5-dibromonaphthalimide it is necessary to use a large excess of aqueous ammonia and to heat at the boil for a long time (up to 2 hours). The 4,5-dichloro- and 4-bromo-5-chloronaphthalimides are obtained in good yields if the reaction is run in the presence of nitrobenzene. Apparently, the imides of the dihalonaphthalic acids are also formed directly through the ammonium salts of the monoamides, since the diammonium salts of the corresponding acids when boiled for 6 hours are converted to the corresponding imides only to the extent of 30–38%.



(I) X = H, Y = H; (II) X = Cl, Y = H; (III) X = Br, Y = H; (IV) X = NO_2, Y = H; (V) X = Cl, Y = Cl; (VI) X = Br, Y = Cl; (VII) X = Br, Y = Br.

EXPERIMENTAL

Naphthalimide (I). A mixture of 50 g of naphthalic anhydride and 80 ml of 16% aqueous ammonia solution was placed in a 200 ml two-necked flask, fitted with stirrer and reflux condenser. The flask with reactants was heated on the water bath for 30 minutes, in such a manner that vigorous boiling of the ammonia solution was avoided. The temperature of the mixture was gradually raised from 60 to 90°. The obtained mass was treated with 50 ml of water, stirred, filtered, the precipitate washed with water, and then dried at 105–110°. Yield 48.7 g, which is 97.9% based on taken, and 99% based on reacted naphthalic anhydride. The obtained naphthalimide proved to be free of the anhydride and other impurities, and did not have to be treated with soda. M.p. 299–300° (corr.), which did not change after repeated recrystallization from nitrobenzene. Acidification of the ammoniacal filtrate gave 0.73 g of naphthalic anhydride.

Naphthalimide is readily soluble in either 5% potassium hydroxide or sodium hydroxide solution at the boil. The corresponding potassium and sodium compounds crystallize from the solutions on cooling, and when treated with water are completely hydrolyzed to naphthalimide.

Potassium salt of naphthalic acid monoamide. A mixture of 5 g of naphthalic anhydride and 8 ml of 16% aqueous ammonia solution was heated at 50–60° for 25–30 minutes, then treated with 50 ml of water, and filtered. To the obtained solution of the ammonium salt of naphthalic acid monoamide was added 50 ml of 30% potassium hydroxide solution. The resulting precipitate was filtered, washed with 20 ml of water, then with 100 ml of alcohol, and dried at 105–110°.

Found %: N 5.43, 5.48. $C_{12}H_6O_3NK$. Calculated %: N 5.53.

4-Chloronaphthalimide (II). A mixture of 30 g of 4-chloronaphthalic anhydride and 45 ml of 16% aqueous ammonia solution was heated on the water bath at 60–90° for 30 minutes. The obtained slurry was treated with 30 ml of water and filtered. The precipitate was washed with water and dried. Yield of (II) 29.3 g (98%). The product was obtained completely pure; m.p. 302–303° (corr.). When boiled with 5% caustic alkali solutions it forms difficultly water-soluble compounds, which do not hydrolyze when treated with water.

4-Bromonaphthalimide (III) was obtained in the same manner as (II). From 30 g of 4-bromonaphthalic anhydride we obtained 29.25 g (98%) of (III). M.p. 296–297° (corr.). When treated with hot 5% caustic alkali solutions it forms difficultly water-soluble compounds, which hydrolyze with ease.

4-Nitronaphthalimide (IV) was obtained in the same manner as (II). From 30 g of 4-nitronaphthalic anhydride we obtained 29.15 g (97.5%) of (IV). The product is quite pure; m.p. 289–290° (corr.). It dissolves with comparative ease in aqueous caustic solutions, forming infusible compounds.

4,5-Dichloronaphthalimide (V). A charge of 20 g of 4,5-dichloronaphthalic anhydride, 20 ml of nitrobenzene and 160 ml of 16% aqueous ammonia solution was placed in a round-bottomed flask fitted with reflux condenser. The mixture was heated on the boiling water bath for 2 hours, after which it was transferred to a beaker, treated with 150–200 ml of 3% sodium hydroxide solution, and boiled until all of the nitrobenzene was removed. The precipitate was filtered and washed with water. It represented the water-insoluble, infusible sodium compound of (V). To isolate the free (V) the precipitate was transferred to a beaker, treated at the boil with 10% hydrochloric acid solution, cooled, filtered, and washed with water. Yield of (V) 17.5 g (88%). M.p. 371–372° (corr.). The compound crystallizes from nitrobenzene as yellow needles with m.p. 372–373° (corr.).

4-Bromo-5-chloronaphthalimide (VI) was obtained from the corresponding anhydride in the same manner as (V). Yield 65%; the compound crystallizes from nitrobenzene as yellow needles. M.p. above 365°. When treated with hot caustic alkali solutions it forms insoluble compounds, which are not hydrolyzed by water.

4,5-Dibromonaphthalimide (VII). A charge of 20 g of 4,5-dibromonaphthalic anhydride and 80 ml of 16% aqueous ammonia solution was placed in a round-bottomed flask and then heated on the boiling water bath for 2 hours. The obtained mixture was transferred to a beaker, 100 ml of 3% sodium hydroxide solution was added, and the mixture boiled for 10 minutes. The precipitate was filtered, washed with water, and dried. Yield of (VII) 19 g (95%). M.p. 341–342° (corr.). The compound crystallizes from nitrobenzene as fine yellow needles with m.p. 343–344° (corr.). When treated with boiling 5% potassium hydroxide solution the compound forms a water-insoluble compound, which in contrast to the sodium compound does not hydrolyze.

SUMMARY

The conditions for the transformation of naphthalic anhydride and its derivatives to the corresponding imides were studied. It was established that the transformation of the anhydride of naphthalic acid proceeds through the formation of an intermediate product—the ammonium salt of naphthalic acid monoamide.

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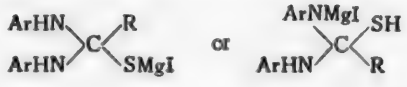
PREPARATION OF DISUBSTITUTED AMIDINES FROM DISUBSTITUTED THIOUREAS AND METHYLMAGNESIUM IODIDE

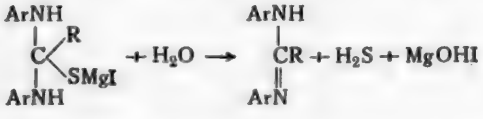
N. V. Koshkin

Several methods have been proposed for the preparation of amidines, of which the main ones for a long time have been those based on the reaction of ammonia with imino esters, imino chlorides or with the esters of orthocarboxylic acids. Recently some methods have been developed for the preparation of amidines from nitriles, cyanides and ammonium salts [1]. Disubstituted amidines of the aromatic series are also obtained in the reaction of organomagnesium compounds with diphenylcarbodiimides, from the anilides of aliphatic acids and aniline, or from a mixture of aliphatic acid and aniline [2].

In this paper we describe methods for the preparation of amidines from N,N'-disubstituted thioureas and methylmagnesium iodide, based on the addition of the organomagnesium compound to the double bond of either the >C = S or the >C = N − group, with the formation of an intermediate compound having the composition



Independent of whether it is the normal or the iso form of the thiourea that reacts with the organomagnesium compound, decomposition of the intermediate compound with water leads to amidine formation according to the equation



Due to the presence of the amidino group in isothioureas, the latter are also capable of forming amidines with sodiomalonic ester. For example, the reaction of N,N'-diphenylthiourea with sodiomalonic ester in benzene solution gives the diethyl ester of (N,N'-diphenylethenylamidine) dicarboxylic acid. Hydrolysis of this compound with alkali leads to the formation of N,N'-diphenylacetamidine

$$C_6H_5NC(NHC_6H_5)CH(COOC_2H_5)_2 \xrightarrow{2H_2O} C_6H_5NC(NHC_6H_5)CH_3 + 2CO_2 + 2C_2H_5OH$$

As a result of our work we prepared N,N'-diphenylacetamidine, N,N'-di(p-tolyl)- and N,N'-di(m-tolyl)-acetamidines, N,N'-di(o-anisidino)-acetamidine and N,N'-allylphenylacetamidine.

EXPERIMENTAL

Preparation of N,N'-diarylacetamidines from N,N'-diarylthioureas and methylmagnesium iodide. The N,N'-diaryl substituted thioureas were obtained for the experiments from the corresponding amines and ammonium thiocyanate by heating the reactant mixture in excess amine at 135−145° for 1.5−2 hours. Instead of ammonium thiocyanate it is also possible to use either thiourea or N-arylthioureas, heating them with aromatic amines, also taken in slight excess, at 145−170°.

An ether solution of methylmagnesium iodide was prepared from 2 g of magnesium and 10 g of methyl iodide in 30 ml of absolute ether. To the flask containing the organomagnesium compound was added in small portions, with mechanical stirring and cooling, 0.07 g-mole of the diarylthiourea, previously dried and pulverized to a fine powder. The addition of the diarylthiourea to the ether solution of the methylmagnesium iodide was accompanied each time by strong frothing of the reactant mixture. After all of the thiourea had been added, the reaction mixture was heated on the water bath for about an hour, after which the ether was distilled off, and the flask contents treated with small portions of either water or dilute hydrochloric acid containing cracked ice. If hydrochloric acid was used to decompose the organomagnesium compound, then the solution was made alkaline by treating with potash. The resulting precipitate of amidine was filtered, washed with water, and recrystallized from a small volume of alcohol.

N,N'-Allylphenylacetamidine. The allylphenylthiourea used for experiment was obtained from allyl mustard oil and aniline. An equimolar mixture of aniline and mustard oil was dissolved in two weight parts of ether and then allowed to stand for a day at room temperature. Coarse, yellow-colored crystals which proved to be insoluble in hot ether were obtained after such standing. After distilling off the ether, the precipitate was recrystallized from chloroform. M.p. 100–101°.

To obtain the allylphenylacetamidine, methylmagnesium iodide was prepared from 20 g of magnesium metal and 100 g of methyl iodide in 250 ml of absolute ether. The organomagnesium compound obtained in this manner was treated in small portions with 33.5 g of allylphenylthiourea with cooling, after which the flask was heated on the water bath for 30 minutes, the ether distilled off, and the flask contents after cooling treated with small portions of water. Aluminum chloride was added to the reaction flask to effect complete solution of the precipitated magnesium hydroxide. The obtained oily liquid was extracted with ether and dried over calcium chloride. Removal of the ether by distillation left an oily residue (13.8 g). Almost complete solution was obtained when the oily liquid was treated with 10% hydrochloric acid solution. The remaining tar was filtered and discarded.

Treatment of the hydrochloric acid solution of the amidine with alkali until alkaline again gave a yellowish oily liquid, readily extracted with ether.

The allylphenylacetamidine forms a salt with concentrated hydrochloric acid.

Found %: N 12.7. $C_{11}H_{14}N_2 \cdot HCl$. Calculated %: N 13.2.

The properties of the obtained N,N'-disubstituted amidines are listed in the table.

TABLE

Name of amidine	Formula of amidine	Melting point	Nitrogen content (in %)		Yield (based on the thiourea) (in %)
			found	calculated	
N,N'-Diphenylacetamidine	$C_{14}H_{14}N_2$	131.5°	13.13	13.32	75
N,N'-Di(p-tolyl)acetamidine	$C_{16}H_{18}N_2$	121	11.40	11.70	50
N,N'-Di(m-tolyl)acetamidine	$C_{16}H_{18}N_2$	104–105	11.26	11.70	60
N,N'-Di(o-anisidino)acetamidine	$C_{16}H_{18}O_2N_2$	137–138	10.15	10.36	52
N,N'-Allylphenylacetamidine (salt)	$C_{11}H_{14}N_2 \cdot HCl$	–	13.20	13.20	41

N,N'-Diphenylacetamidine from sodiomalonic ester and diphenylthiourea. The sodiomalonic ester was prepared from 12 g of malonic ester and 1.7 g of sodium metal in 150 ml of dry benzene with stirring and heating at 60–70°. The ester obtained in this manner was treated with 16 g of dry, finely divided diphenylthiourea, and the mixture heated for 6–8 hours at the boil. Then the benzene was distilled off, and the obtained precipitate was heated for 2 hours with 150–200 ml of cold-saturated alcoholic caustic solution. On conclusion of heating the solution was treated with water, and the obtained precipitate was filtered, washed with water, and recrystallized from alcohol. Yield 10 g. M.p. 131°.

Found %: N 13.20. $C_{14}H_{14}N_2$. Calculated %: N 13.32.

SUMMARY

1. Methods were proposed for the preparation of N,N'-diphenylacetamidine, N,N'-di(p-tolyl)acetamidine, N,N'-di(m-tolyl)acetamidine, N,N'-di(o-anisidino)acetamidine and N,N'-allylphenylacetamidine from methylmagnesium iodide and disubstituted thioureas.

2. N,N'-Diphenylacetamidine was also obtained by the reaction of sodiomalonic ester with diphenylthiourea.

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Leningrad Technological Institute of the Food Industry Received June 8, 1957

ACTION OF γ-RADIATION OF RADIOACTIVE COBALT (Co^{60}) ON AQUEOUS SOLUTIONS OF AROMATIC HYDROCARBONS

M. A. Khenokh and E. M. Lapinskaia

In aqueous solutions of organic compounds, in particular of hydrocarbons and their derivatives, ionizing radiation causes complex chemical transformations [1–7]. At the present time it is believed that the action of ionizing radiations on aqueous solutions is due to the radiolytic cleavage of the water into hydrogen atoms and free OH and O_2H radicals, with the formation of H_2 and H_2O_2 as the final products [8]. The oxidation of organic compounds that occurs here depends on the reaction of these radicals with the dissolved substance similar to the action of Fenton reagent ($H_2O_2 + Fe^{2+}$ mixture) [6a, 9]. Continuing our earlier studies of the effect of ionizing radiations [10, 11] and ultrasonic waves [12–15] on organic compounds, we subjected saturated aqueous solutions of chemically pure benzene and toluene, and of 0.01 M solutions of phenol, to the action of Co^{60} γ-rays (~ 2 curies) at 15 ± 2°.

To prepare the solutions we always used triple-distilled water. The experiments were repeated at least 3–5 times. The method of irradiation was described earlier [10a]. An SF-4 spectrophotometer was used to measure the absorption spectra, using a cuvette and a layer thickness of 5 mm. Formaldehyde [16] and the phenols [17, 18] were determined by the earlier described methods [13a]. The amount of radiation absorbed by the liquid was determined from the amount of $FeSO_4$ oxidized in 0.8 N H_2SO_4 solution in the presence of dissolved air. The Fe^{2+} concentration was determined by potentiometric titration with 0.01 N $KMnO_4$ solution. The original $FeSO_4$ concentration was $2.02 \cdot 10^{-3}$ M. The yield of oxidized iron was taken equal to 15.5 molecules per 100 ev [8].

Action of γ-rays on benzene solutions. The results obtained in the spectrophotometric measurement of irradiated benzene are shown in Fig. 1. An examination of the curves in Fig. 1 reveals that the exposure of benzene solutions to γ-rays results in an increased absorption of ultraviolet light. However, here the position of the maxima in the 230–260 mμ region is retained when compared with the spectrum of the original benzene solution, and new maxima do not appear. After irradiation the spectrum expands in the long-wave portion and embraces the region up to 280 mμ, in which connection sharp new absorption bands arise at 269 and 276 mμ. They indicate the formation of phenol [19]. In addition, a new absorption region appears (305–380 mμ) with a maximum at 348 mμ. The hydroxylation of benzene and the resulting formation of phenol are the result of the action of the free radicals that arise in the radiolysis of water under the influence of γ-rays [4]. The influence of the radiation dose on the formation of phenol in benzene solutions is shown in Fig. 2, from which it can be seen that the amount of phenol increases with increase in the dosage. The yield of phenol is 1.31 molecules/100 ev, which coincides with the literature data [20]. The oxidative processes that take place under the influence of γ-rays also cause decomposition of the benzene ring; formaldehyde was found in the reaction products. The amount of formaldehyde increases with increase in the radiation dose (Fig. 2). However, the yield of the product is very small–0.07 molecules/100 ev.

Similar changes in benzene solutions can also be obtained chemically by treating the benzene solution with Fenton reagent. According to the literature, Fenton solution causes the formation of phenol and polyphenols in benzene solutions [21]. To characterize the products that originate in a benzene solution when treated with Fenton reagent, we ran some experiments in which an increasing amount of H_2O_2 and a constant amount of $FeSO_4$ were added to a constant volume of benzene. The final volume of the mixture was made up to 10 ml by the addition of water. The solutions were allowed to stand for 24 hours at 15 ± 2°, after which they were subjected

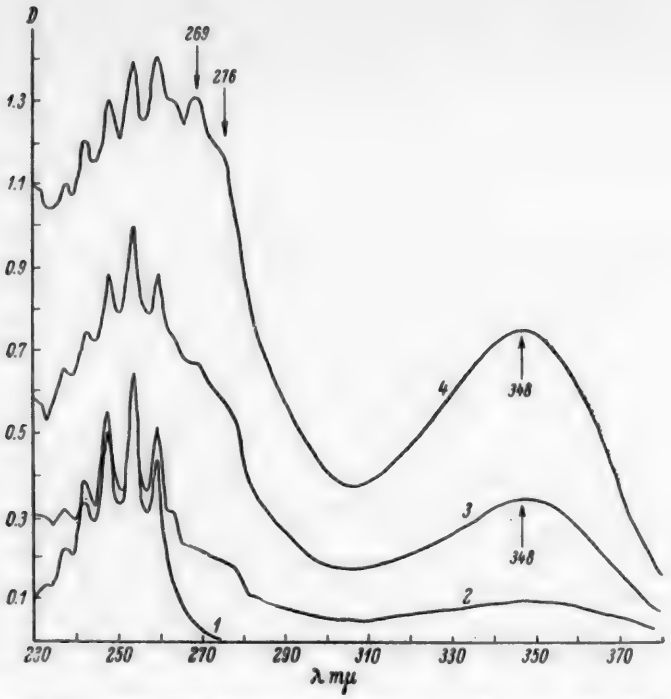

Fig. 1. Absorption spectra of benzene solutions irradiated with γ-rays. 1) Not irradiated, 2) irradiated with a dose of $0.9 \cdot 10^{19}$ ev/ml, 3) with a dose of $2.1 \cdot 10^{19}$ ev/ml, 4) with a dose of $3 \cdot 10^{19}$ ev/ml.

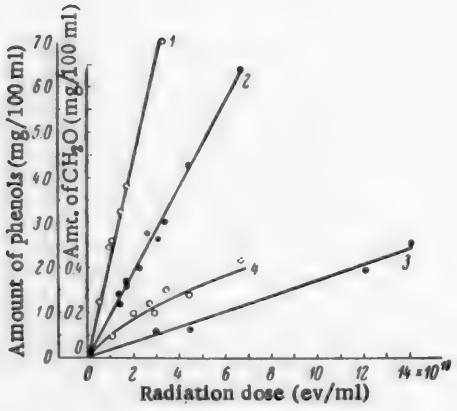

Fig. 2. Effect of the γ-radiation dose on the amount of products formed.
1) Of phenols in benzene solution, 2) of phenols in toluene, 3) of formaldehyde in benzene solution, 4) of formaldehyde in toluene solution. Strength of dose $\sim 4.5 \cdot 10^{19}$ ev/ml · sec.

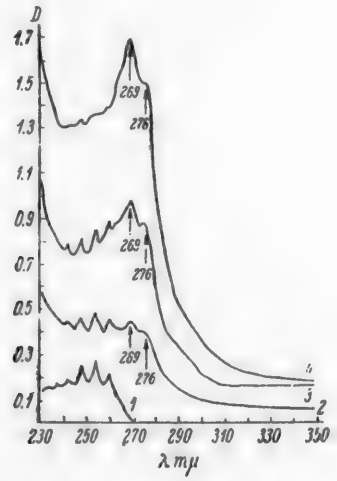

Fig. 3. Absorption spectra of benzene solutions subjected to the action of Fenton reagent ($5.5 \cdot 10^{-4}$ M Fe^{2+}).
1) Original benzene solution, 2) $5.9 \cdot 10^{-4}$ M. H_2O_2, 3) $14.7 \cdot 10^{-4}$ M. H_2O_2, 4) $29 \cdot 10^{-4}$ M. H_2O_2.

to spectrophotometry. The obtained data are shown in Fig. 3. From the curves it can be seen that the action of Fenton reagent, the same as that of γ-radiation, is to cause in benzene solutions an increase in the absorption intensity of ultraviolet light and the appearance of new absorption bands with λ_{max} at 269 and 276 mμ, characteristic for phenol. In contrast to the action of γ-rays, the action of $H_2O_2 + Fe^{3+}$ failed to cause absorption of ultraviolet light in the region of greater wavelengths (305–380 mμ). As a result, in contradiction to the literature, our experiments indicate that the products, obtained in the action of γ-rays on aqueous solutions of benzene and those obtained by decomposition with H_2O_2 in the presence of $FeSO_4$ [6a], are not completely identical.

Action of γ-rays on toluene solutions. The curves for the absorption of ultraviolet light by toluene solutions are shown in Fig. 4. From Fig. 4 it can be seen that an increase in the total absorption occurs under the influence of γ-rays. Here the maxima at 261 and 268 mμ are also retained after irradiation. New bands do not appear in the 230–270 mμ region. Additional absorption arises in the 320–380 mμ region with λ_{max} at 353–354 mμ.

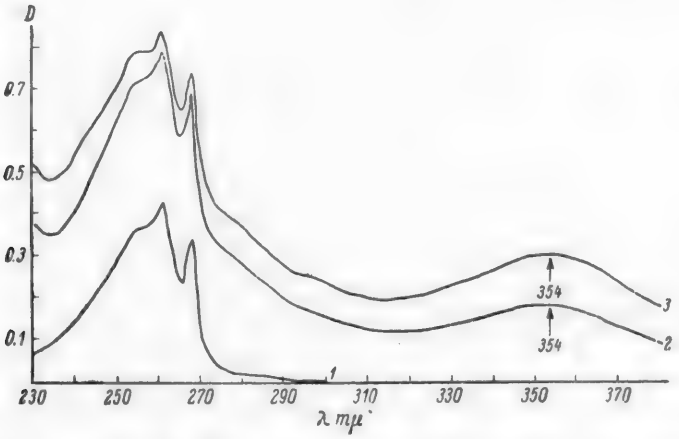

Fig. 4. Absorption spectra of toluene solutions irradiated with γ-rays. 1) Not irradiated, 2) irradiated with a dose of $1.46 \cdot 10^{19}$ ev/ml, 3) with a dose of $2.56 \cdot 10^{19}$ ev/ml. Strength of dose $6.1 \cdot 10^{18}$ ev/ml · sec

Chemical analysis indicates that toluene in aqueous solutions under irradiation suffers oxidative destruction with the formation of formaldehyde. The influence of the dose on the amount of formaldehyde formed as shown in Fig. 2, from which it can be seen that the amount of formaldehyde increases with increase in the radiation dose. The yield of formaldehyde is 0.17 molecules/100 ev. The formation of phenols here (Fig. 2) in a yield of 0.56 molecules/100 ev indicates that, together with decomposition processes, there occurs transformation of the toluene into a new compound with retention of the six-membered ring. Analysis shows that hydroxylation of the six-membered ring is accomplished with greater ease than is the formation of formaldehyde.

After irradiation of the toluene solutions, the same as in the case of benzene, the value of the pH dropped. A dose of $2.88 \cdot 10^{19}$ ev/ml caused the pH of the toluene solutions to drop from 6.0 to 3.98. A comparison of the yields of formaldehyde and phenolic compound in irradiated benzene and toluene solutions reveals that the profound destruction processes, causing the formation of formaldehyde, proceed with greater intensity in toluene than in benzene (Fig. 2); at the same time toluene suffers less hydroxylation than does benzene (Fig. 2). Evidently, this is due to the presence of the CH_3 group in toluene. The former, suffering chemical changes under the influence of ionizing radiation, diverts a part of the free radicals and in this way protects the six-membered ring from hydroxylation.

The action of Fenton reagent on toluene solutions revealed that the changes occurring here differ from those obtained in the exposure to γ-rays. The absorption spectra of the toluene solutions treated with Fenton reagent are shown in Fig. 5, from which it can be seen that with increase in the amount of H_2O_2 in Fenton reagent the action of the free radicals causes an increase in the absorption density in toluene solutions. Here

the ultraviolet light absorption maxima at 261 and 268 mμ vanish, and new, ill-defined maxima appear at 248, 253 and 276 mμ. Absorption is absent in the 300–360 mμ region.

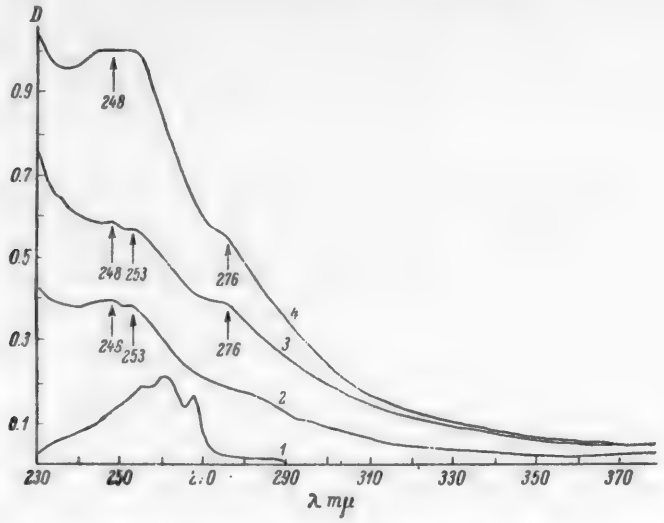

Fig. 5. Absorption spectra of toluene solutions treated with Fenton reagent ($5.5 \cdot 10^{-4}$ M Fe^{3+}). 1) Original toluene solution, 2) $5.9 \cdot 10^{-4}$ M. H_2O_2, 3) $14.7 \cdot 10^{-4}$ M. H_2O_2, 4) $23.5 \cdot 10^{-4}$ M. H_2O_2.

Action of γ-rays on phenol solutions. From the curves shown in Fig. 6 it can be seen that irradiation exerts very little influence on the absorption spectrum of phenol. With increase in the dose only slight increase in the absorption occurs in phenol solutions and the absorption maxima at 269 and 276 mμ are retained. However, it is indicated in the literature that phenol under the action of ionizing radiation can undergo transformation with the formation of quinone, catechol and other products [4]. As can be seen from Fig. 6, the absorption spectrum in the 230–300 mμ region does not reflect any changes in aqueous phenol solutions when exposed to γ-rays. Experiments with Fenton reagent revealed that increasing the H_2O_2 concentration in the reagent only led to a slight increase in the ultraviolet absorption without changing the characteristic spectrum of phenol. When the spectra of irradiated benzene, toluene and phenol (Figs. 1, 4 and 6) are compared, it can be seen that the least changes under the influence of γ-rays, and also of Fenton reagent, occur in the spectrum of phenol. This shows that changes in the absorption spectra of irradiated solutions of aromatic hydrocarbons depend on the character of the substituent in the six-membered ring.

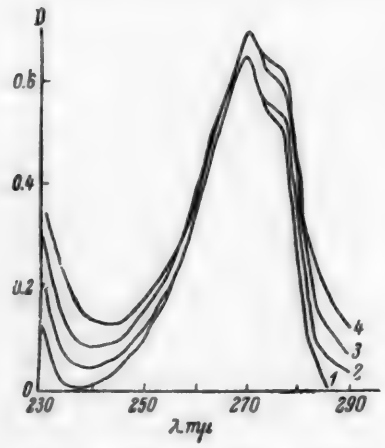

Fig. 6. Absorption spectra of phenol solutions irradiated with γ-rays. 1) Not irradiated, 2) irradiated with a dose of $4.92 \cdot 10^{19}$ ev/ml, 3) with a dose of $7 \cdot 10^{19}$ ev/ml, and 4) with a dose of $8.99 \cdot 10^{19}$ ev/ml. Strength of dose $6.1 \cdot 10^{15}$ ev/ml · sec.

Some authors believe it possible to assume that the mechanism of the chemical action of ionizing radiation in aqueous solutions is similar to that of the chemical influence exerted by ultrasonic waves [8a, 22–24]. The results of the present study also show that in irradiation the character of the changes in hydrocarbons is similar to their transformations under the influence of ultrasound [13a]. In both cases hydroxylation of the six-membered ring occurs in the hydrocarbon solutions,

and also its destruction with the formation of formaldehyde. However a comparison of the spectra of irradiated and ultrasonically treated solutions of benzene and toluene reveals that γ-rays cause changes in these solutions that are sharply different from those evoked by ultrasonic treatment [13a]. Phenol solutions represent an exception which, judging by the spectra, proved to be equally stable toward both γ-rays and ultrasonic waves. The obtained material suggests that the chemical action of ionizing radiations differs from the reactions that proceed in aqueous solutions under the influence of an ultrasonic field. This conclusion is supported by earlier published studies [10–15].

SUMMARY

1. The action of the γ-radiation of radioactive cobalt (Co^{60}) on aqueous solutions of benzene, toluene and phenol was studied.

2. It was shown that when benzene solutions are exposed to γ-rays the six-membered ring suffers hydroxylation to give phenol in a yield of 1.31 molecules/100 ev, and also that it suffers destruction with the formation of formaldehyde in a yield of 0.07 molecules/100 ev. After irradiation the spectrum of benzene showed absorption in the 305–380 mμ region with a maximum at 348 mμ.

3. In toluene solutions irradiation was accompanied by the formation of a phenolic compound in a yield of 0.56 molecules/100 ev and of formaldehyde in a yield of 0.16 molecules/100 ev. Exposure to γ-rays failed to produce any changes in the 230–280 mμ region of the toluene spectrum, but after such exposure absorption appeared in the wavelength region 320–380 mμ with a maximum at 353–354 mμ.

4. Exposure to γ-rays failed to exert any noticeable influence on the absorption spectrum of phenol solutions.

5. The absorption spectra of benzene and toluene solutions that had been treated with Fenton reagent differ from the spectra of the irradiated solutions. In the case of benzene solutions the differences in the absorption bands appear in the 305–308 mμ region, while in the case of toluene solutions they are found in the entire region investigated (230–380 mμ).

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CHANGE IN PROTEINS AND AMINO ACIDS UNDER THE INFLUENCE OF ULTRASONIC VIBRATIONS

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Earlier it had been shown that the exposure of aqueous solutions to ultrasonic vibrations causes the decomposition of high-molecular carbohydrates, saccharides, gelatin and amino acids [1–4]. Bearing in mind the scientific and practical importance assumed by ultrasonic vibrations (USV) in chemistry, it seemed of interest to expand the investigations on the influence of ultrasonics on proteins and amino acids. Literature sources indicate that proteins suffer various physicochemical changes when exposed to USV [5,6], while here amino acids suffer decomposition with the formation of aldehydes, ammonia and other compounds [3, 7, 8]. However, the published data are far from adequate to permit judging as to the new products that arise here, or as to the transformations suffered by these substances under ultrasonic treatment.

In this communication, being a continuation of our investigations on the influence exerted by ultrasonic vibrations [1–4, 9, 10] and by nuclear radiations [11, 12] on high-molecular compounds and their elementary units, we give the results of our experiments on the ultrasonic treatment of proteins, and of aliphatic and aromatic amino acids. For the experiments we took 25 ml portions of $2 \cdot 10^{-2}$–$2 \cdot 10^{-3}$ M solutions of the amino acids and 0.5% solutions of the proteins: egg albumin (Kahlbaum), photogelatin, containing 0.054% ash after purification (by the Lebu method), and casein (by the Hammersten method), prepared using 0.1% soda solution, and exposed them at 38–40° to ultrasonic vibrations with a frequency of 435 kc.

To determine phenolic hydroxyls we used the method described in [10]; ammonia was determined by the diffusion method [13]. The relative viscosity was measured in an Ostwald viscosimeter at 25°, and the pH was determined using a glass electrode. An SF-4 spectrophotometer was used to take the absorption spectra. For the chromatographic analysis we used Factory No. 2 chromatographic paper. As solvent we used a mixture of n-butyl alcohol, acetic acid and water (5 : 4 : 1). As developer we used a 0.1% solution of ninhydrin in alcohol. For the quantitative chromatographing we used a 0.5% solution of ninhydrin in acetone [14]. The colored stains were cut out and extracted for about 5 hours in a test tube, in the dark, with 8 ml of 70% alcohol, previously saturated with $CuSO_4$. The obtained solutions were subjected to spectrophotometric measurement at λ 540 mμ, in a cuvette with a layer thickness of 5 mm, and a slit opening of 1.7 mm (as compared to alcohol in the reference cuvette). The change in the amino acid concentration in the solutions exposed to ultrasonic treatment was determined by the change in the absorption density, using that of the original amino acid concentration as a base. To quantitatively determine phenylalanine, tyrosine and tryptophan, we cut out from the chromatograms at the R_f level of the shown amino acid stains the corresponding adjacent portions, which were then eluted with 5 ml portions of 0.1 N HCl. The concentration of the aromatic amino acids was calculated from the decrease in absorption at λ_{max} in a cuvette with a layer thickness of 10 mm and using 0.1 N HCl as a comparison standard. The distribution of the aromatic amino acids on the chromatogram was also shown using an ultrachemiscope* with an UFS-2 filter. Histidine was determined using diazotized sulfanilic acid and spectrophotometric measurement of the solutions at λ 530 mμ (slit opening 1.4 mm) and a layer thickness of 5 mm [15]. Cysteine and cystine were determined by reduction with phospho-18-tungstic acid [13]. The spectrophotometric measurement of the solutions was made at λ 740 mμ [16] in a cuvette with a layer thickness of 4 mm and a slit opening of 0.04 mm. The amount of cystine, formed from cysteine under ultrasonic treatment, was determined from the difference in the concentrations, found when the reaction was

*As in original—Publisher's note.

run in the presence of Na_2SO_3 and in its absence. Triple-distilled water was used in all of the experiments. The experiments were repeated at least 3–5 times. A description of the high-frequency generator used and the conditions of operation were given earlier [3,4].

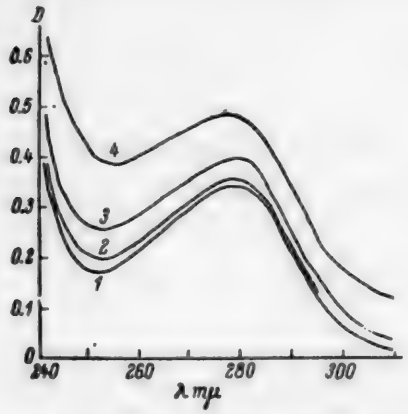

Fig. 1. Absorption curves of albumin solutions (c = 0.5%, d = 1 mm). 1) Not treated with ultrasonics, 2) treated with ultrasonics for 1 hour, 3) 3.5 hours, 4) 5 hours.

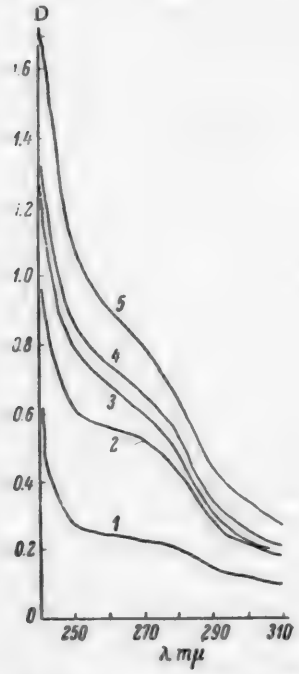

Fig. 2. Absorption curves of gelatin solutions (c = 0.5%, d = 4 mm). 1) Not treated with ultrasonics, 2) treated with ultrasonics for 3 hours, 3) 5 hours, 4) 7 hours, 5) 10 hours.

Action of ultrasonics on solutions of albumin, casein and gelatin. The results of the spectrophotometric measurement of ultrasonorated albumin solutions are shown in Fig. 1. An examination of the curves reveals that the protein absorption in the 230–300 mμ region increases with increase in the time of ultrasonic treatment. However, new absorption maxima do not appear, and the curves retain their original character. A similar change in the absorption was also observed when casein solutions are exposed to ultrasonic vibrations. The absorption spectrum of gelatin (Fig. 2), due to the absence of tryptophan and a reduced amount of other aromatic amino acids in it [17], differs sharply from the spectra of both albumin and casein. From Fig. 2 it can be seen that exposure of gelatin solutions to ultrasonic vibrations causes an increase in the absorption of ultraviolet light. Here after 3-hour exposure a bulge appears on the absorption curves in the 250–290 mμ region, which then levels out with further ultrasonic exposure.

The spectrophotometric analysis data obtained for the solutions of albumin, casein and gelatin do not permit judging as to the nature of the new compounds formed during ultrasonic exposure; however, the obtained curves do serve as evidence that changes occur in protein molecules when they are exposed to USV. In order to determine more accurately the physicochemical changes that take place in protein solutions when exposed to ultrasonics, we investigated the effect of USV on gelatin. From the curves in Fig. 3 it can be seen that in the case of 0.5 and 1% gelatin solutions, exposed to ultrasonic action, the viscosity drops. The character of the curves indicates that the viscosity strives to reach a certain state, which does not change when the time of ultrasonic exposure is increased. For the 0.5% gelatin solution such a state is attained after 2-hour exposure to USV, and for the 1% solution it is attained after exposure to USV for 7–8 hours. A second measurement of the viscosity, made for the 0.5% gelatin solutions after being kept for 16 hours at 19 ± 2°, revealed that even after aging the viscosity of the gelatin that had been exposed to ultrasonics for 1 hour was 52% less than the viscosity of the original solution. The irreversible decrease in the viscosity indicates that together with the mechanical effect, exposure to ultrasonic vibrations causes chemical processes, leading to the decomposition of protein molecules.

Earlier it was established that the cleavage of ammonia and the formation of formaldehyde occur here [3]. Ultrasonic treatment of gelatin solutions is

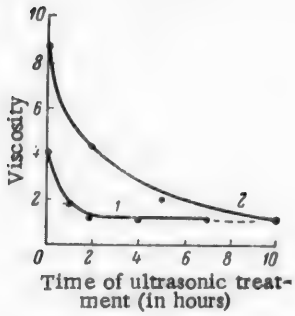

Fig. 3. Change in the relative viscosity of gelatin when exposed to ultrasonic treatment. 1) 0.5% solution, 2) 1% solution.

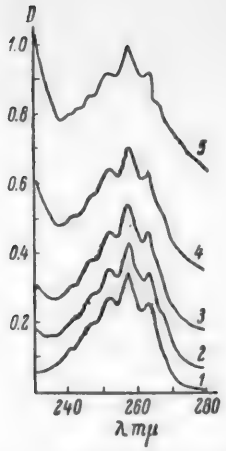

Fig. 4. Absorption curves of phenylalanine ($c = 2 \cdot 10^{-2}$ M, d = 1 mm). 1) Not treated with ultrasonics, 2) treated with ultrasonics for 0.5 hour, 3) 1 hour, 4) 2 hours, 5) 4.5 hours.

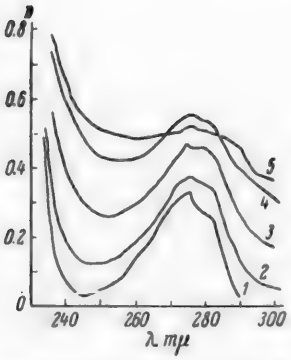

Fig. 5. Absorption curves of tyrosine solutions ($c = 2.2 \cdot 10^{-3}$ M, d = 1 mm). 1) Not treated with ultrasonics, 2) treated with ultrasonics for 2 hours, 3) 5 hours, 4) 10 hours, 5) 17 hours.

accompanied by a decrease in the pH, but to a lesser extent than in the case of pure water. After exposure to ultrasonics for 4 hours the pH decrease in water was 48.2% of the original value (pH 6.2), whereas when 0.25, 0.5 and 1% gelatin solutions were exposed to ultrasonics for the same length of time the pH decrease was respectively 25.8, 16.1 and 11.3%. The decrease in pH shown by water solutions when exposed to ultrasonics is due to the oxidative effect of cavitation, causing the formation of HNO_2 and HNO_3 [3,5]. As the protein concentration is increased the buffering action of the solution is also increased, which apparently hinders change in the pH.

Action of ultrasonics on amino acid solutions. To obtain a better idea of the transformations that take place in proteins when exposed to ultrasonic waves, we investigated the action of ultrasonics on amino acids. Since the absorption shown by proteins in the ultraviolet portion of the spectrum is mainly due to the presence of aromatic amino acids in the macromolecules, it seemed of interest to first determine the effect of USV on the change in the absorption of the indicated amino acids. The results obtained when ultrasonorated solutions of phenylalanine ($2 \cdot 10^{-2}$ M), tyrosine ($2.2 \cdot 10^{-3}$ M) and tryptophan ($2 \cdot 10^{-3}$ M) were subjected to spectrophotometric measurement are shown in Figs. 4–6. The curves show that the absorption of ultraviolet light in phenylalanine (Fig. 4) and tyrosine (Fig. 5) solutions increases as the time of exposure to ultrasonic treatment is increased. However, here new absorption maxima are not formed. The absorption curves probably also reflect the absorption of light by the products formed during ultrasonic treatment. Consequently, the measured absorption density is apparently the sum of the absorption shown by the still undecomposed molecules of the original substance and the newly formed compounds.

The absorption spectra of phenylalanine and tyrosine, isolated by chromatographing the ultrasonically treated solutions, revealed a reduction in the absorption of ultraviolet light, which permitted the conclusion that the amino acids had undergone partial decomposition. Quantitative data on the change in the concentrations of these amino acids are shown in the Table.

TABLE

Time of ultrasonic treatment (in hours)	Concentration of amino acid (in mole/liter)		
	phenylalanine ($\times 10^2$)	tyrosine ($\times 10^3$)	tryptophan ($\times 10^3$)
Not treated with ultrasonics	2.0	2.2	2.0
3	–	–	1.17
5	–	–	0.65
6.5	–	1.76	–
8	1.7	–	–
10	–	1.39	0.54
15	–	–	0.35
17	–	1.12	–
19	1.2	–	–

In tryptophan solutions, the same as in the case of phenylalanine and tyrosine, new absorption maxima fail to be formed as the result of exposure to ultrasonics. However, the absorption drops in solutions of this amino acid as the time of exposure to ultrasonic treatment is increased (Fig. 6). Evidently, the destruction products of tryptophan either have a slight absorption value or do not absorb at all in the indicated region of the spectrum (230–300 mμ), and consequently the substances formed here do not increase the absorption of the solutions. The change in the amount of tryptophan, separated from the transformation products by chromatographing, is shown in the Table, from which data it is obvious that ultrasonic treatment leads to decomposition of the amino acid.

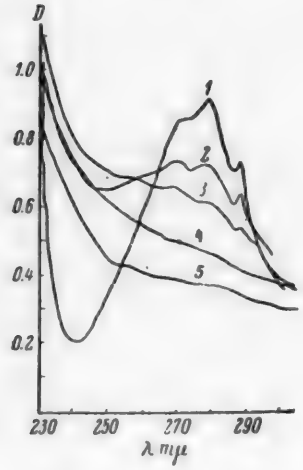

Fig. 6. Absorption curves of tryptophan solutions (c = $= 2 \cdot 10^{-3}$ M, d = 1 mm). 1) Not treated with ultrasonics, 2) treated with ultrasonics for 3 hours, 3) 5 hours, 4) 10 hours, 5) 15 hours.

The oxidative processes, occurring in aqueous solutions under the influence of ultrasonics, cause various chemical transformations in the aromatic amino acids. In phenylalanine solutions exposure to ultrasonics results in the evolution of ammonia and hydroxylation of the benzene ring. Figure 7 shows that both deamination and the formation of phenolic hydroxyls increase with increase in the time of exposure to USV. This means that together with destruction of the NH_2 group, phenylalanine is converted to a new compound with retention of the six-membered ring. The decomposition of aromatic amino acids when exposed to ultrasonics is accompanied by the formation of new products, giving a color test with ninhydrin. The chromatograms of phenylalanine (R_f = 0.65) solutions that had been treated with ultrasonics for 10 hours showed five stains with R_f = 0.50 and 0.40. Ultrasonic exposure for 15 hours caused the additional formation of stains with R_f = 0.30 and 0.08. Chemical changes in tyrosine (R_f = 0.51) solutions after exposure to USV for 5–17 hours resulted in the appearance of a stain with R_f = 0.30 on the chromatogram of the amino acid. The eluate, obtained from the paper cut out from the corresponding portion of the chromatogram at the level of this colored stain, absorbed ultraviolet light in the 270–300 mμ region with the maximum absorption at 282 mμ. On increasing the time of exposure of the tyrosine solution to ultrasonics the density of ultraviolet light absorption in the eluate decreased, indicating decomposition of the new compound formed in the ultrasonic treatment of tyrosine. Identification of the stains appearing on the chromatograms will be the subject of further studies.

Histidine suffers decomposition when exposed to ultrasonics. Exposure of $1 \cdot 10^{-2}$ M solutions of the amino acid to USV for 5, 10 and 15 hours caused decomposition of the histidine to the extent of 18, 38 and 53%, respectively. It is the imidazole ring that is destroyed here, since the reaction with diazobenzenesulfonic acid steadily gave a weaker color, characteristic for the presence of the imidazole ring, as the time of histidine exposure to ultrasonics was increased.

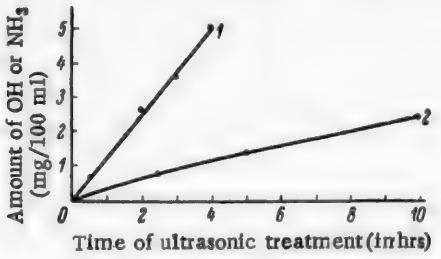

Fig. 7. Effect of ultrasonic treatment on the formation of phenolic hydroxyls (1) and deamination (2) in $2 \cdot 10^{-2}$ M phenylalanine solutions.

The chemical processes occurring during ultrasonic exposure also produce changes in the solutions of aliphatic amino acids. The curves in Fig. 8 show that the extent of amino acid decomposition increases as the time of exposure to ultrasonics is increased. The longer the chain in the amino acid, the more extensive is the decomposition of the amino acid with the formation of ammonia and formaldehyde [3]. With the same exposure time, for example after 10 hours of ultrasonic treatment, the decrease in the amounts of alanine, valine and n-leucine was respectively 9, 59 and 75% of the original. The chromatographic analysis results revealed that the destruction of aliphatic amino acids is accompanied by the formation of new products, giving stains when the paper is developed with ninhydrin.

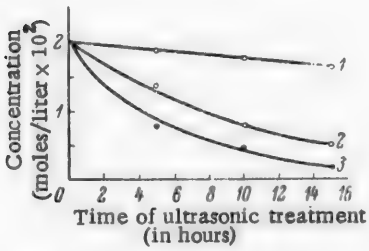

Fig. 8. Decomposition of aliphatic amino acids when exposed to ultrasonics. 1) alanine, 2) valine, 3) n-leucine.

Rupture of the CO—NH bond occurred when 0.013 M solutions of hippuric acid were exposed to ultrasonic treatment for 10—15 hours. The chromatograms of solutions treated in this manner showed a stain, from its position corresponding to that of glycine. The presence of the latter was confirmed by chromatographing the ultrasonorated solutions in two different solvents (butyl alcohol, acetic acid and water, and phenol that had been saturated with water in an atmosphere of ammonia). Together with hydrolysis, hippuric acid also suffered hydroxylation during ultrasonic treatment. After exposure to USV for 3 and 6 hours the solutions of hippuric acid were found to contain respectively 1.7 and 3.1 mg of OH groups per 100 ml of solution.

Exposure to USV also causes chemical transformations in solutions of sulfur-containing amino acids. The results obtained in the ultrasonic treatment of solutions of cysteine and cystine are shown in Fig. 9, from which it can be seen that the decomposition of cysteine increases with increase in the time of exposure to ultrasonics, and reaches nearly 100% after exposure for 13 hours (Curve 1). The oxidative processes that occur here cause transformation of the cysteine to cystine. Curve 2 (Fig. 9) shows that the formation of cystine increases at first, and then, as the time of exposure is increased, it decreases. The latter suggests that USV exerts a destructive action on cystine. This is also supported by Curve 3 in Fig. 9.

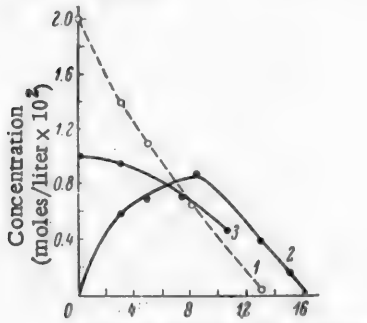

Fig. 9. Effect of ultrasonic treatment on the change in the concentration of cysteine and cystine. 1) decomposition of cysteine, 2) formation of cystine from cysteine, 3) decomposition of cystine.

To establish the influence exerted by the HNO_2, HNO_3 and H_2O_2 [5], formed in water when the latter is

exposed to ultrasonic treatment, on the decomposition of amino acids, we prepared solutions of the latter using water that had been previously exposed to USV for 15 hours. After being kept at 38–40° for 10–15 hours the solutions were subjected to chromatographic analysis. However, except for the stains showing the location of the deposited amino acids, the chromatograms failed to show any new stains. Evidently, destruction of aliphatic amino acids is not caused by H_2O_2, HNO_2 and HNO_3, but instead depends on the oxidative action exerted by the free radicals arising in the ultrasonic field from the decomposition of water ($H_2O \rightarrow H + OH$) [5]. However, in the case where hippuric acid solutions were prepared using ultrasonorated water, and then kept under the above indicated conditions, analysis revealed that a stain appeared on the chromatogram, from the R_f "evidence" corresponding to free glycine. This permits the conclusion that the formation of the acids HNO_2 and HNO_3 also exerts an influence on the decomposition of hippuric acid in an ultrasonic field, causing hydrolytic cleavage of the –CO–NH– bond.

The results of the present study show that the action of USV causes substantial chemical changes in solutions of proteins and amino acids. The obtained material makes it possible to conclude that in some cases the effect of ultrasonic treatment is similar to the action of ionizing radiations on the same aqueous systems. Thus, in both cases the change in the spectra of proteins and aromatic amino acids has a similar character [12b]. When exposed to ultrasonic waves, the same as when exposed to γ-rays, amino acids show ammonia evolution, destruction of the carbon chains with cleavage of the carbon as formaldehyde, and hydroxylation of the six-membered ring in the case of aromatic amino acids [3, 12a, 12b]. A comparison of the data obtained in ultrasonic treatment with that obtained using ionizing radiation also shows that ultrasonic vibrations exert a specific influence on solutions of amino acids and other compounds [2b, 11b]. For example, the formation of NH_3 and H_2CO in the destruction of amino acids when exposed to ultrasonic waves increases with increase in the length of the amino acid chain [3], whereas in the case of radiolysis, on the contrary, the shorter the carbon chain, the greater the amount of the above indicated decomposition products formed [12a]. Finally, differences in the character of the absorption spectra of aqueous solutions of benzene and toluene after exposure to ultrasonics [10] or to the action of γ-rays [12b] permit assuming that the six-membered rings of aromatic amino acids suffer dissimilar transformations under the influence of the mentioned physical agents. As a result, the analogy cited by some authors between the chemical action of ultrasonic waves and that of ionizing radiations on the basis that free radicals [5] are formed in aqueous solutions under their influence, in our opinion, can have only limited significance, since it was experimentally shown that the products, arising in the exposure to ultrasonic waves and to nuclear radiation, are different.

SUMMARY

1. The action of ultrasonic vibrations was studied on solutions of albumin, casein, gelatin, and aliphatic and aromatic amino acids. It was shown that protein solutions under the influence of ultrasonic vibrations show increased absorption of ultraviolet light in the 230–300 mμ region without the formation of new absorption bands. In gelatin solutions the action of ultrasonic vibrations caused irreversible change in the viscosity, a fall in pH, and decomposition of the molecule with the formation of ammonia and formaldehyde.

2. Ultrasonic vibrations cause the decomposition of aromatic amino acids.

3. It was shown that the longer the chain, the greater the tendency shown by aliphatic amino acids to decompose under the influence of ultrasonic vibrations.

4. The action of ultrasonic vibrations leads to decomposition of the imidazole ring in histidine and to rupture of the CO–NH bond in benzoylglycine (hippuric acid) with liberation of the amino acid. The oxidative action of ultrasonic vibrations causes destruction of cysteine with the formation of cystine which, however, on further ultrasonic treatment also suffers decomposition.

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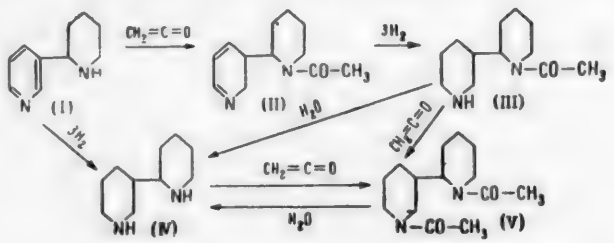
REACTION OF KETENE WITH NITROGEN-CONTAINING BASES

V. ACETYLATION OF BIPIPERIDINE WITH KETENE

Iu. V. Svetkin

In the previous communication [1] it was shown that ketene can be successfully used for the acetylation of certain alkaloids. Especially good results are obtained if the reaction is run with the additions of either acetic acid or water. Later this method was extended to derivatives of the bipiperidine series, the reactivity of which toward ketene has not been studied up to now. In addition, it seemed interesting to incidentally touch upon the subject of the structure of ammodendrine. As is known, this alkaloid was first isolated by Orekhov and Proskurnina [2] from Ammodendron conollyi Bge. Ammodendrine is a secondary base, has one double bond, and an acetyl radical. Orekhov and Proskurnina [3], by hydrogenating ammodendrine obtained dihydroammodendrine, which was then methylated. Subsequent saponification of the methyl derivative showed the position of the acetyl group, whereas the position of the ethylene bond was determined only tentatively. Recently Schopf and Braun [4] in decomposing N-acetylisotripiperidine with hydriodic acid obtained ammodendrine, and in this way rigidly proved the position of the double bond in this alkaloid.

We subjected anabasine and its derivatives to hydrogenation and incidentally studied dihydroammodendrine. The whole cycle of the transformations involved is shown in the scheme below.



The product (III) (monoacetylbipiperidine) obtained by us had constants different from those of dihydroammodendrine, and this served as additional evidence that the formula proposed by Schopf and Braun for ammodendrine is correct. On the other hand, as the result of our work it was established that ketene in the presence of CH_3COOH readily acetylates bipiperidine and its derivatives.

EXPERIMENTAL

Hydrogenation of acetylanabasine (II). Acetylanabasine was obtained by the acetylation of anabasine (I) with ketene in the presence of acetic acid. The hydrogenation of acetylanabasine was run in the following manner. Ten grams of acetylanabasine with b.p. 198–200° (5 mm) and $n^{20}D$ 1.5541 was added to 200 ml of boiling anhydrous alcohol. Then 24 g of sodium metal was added to the reaction mixture through the reflux condenser. On conclusion of reaction the mixture was treated with hydrochloric acid until acid, and then the alcohol was removed by vacuum-distillation. Yield of N-monoacetyl-α,β-bipiperidine 1.3 g (12.6%).

B.p. 130–132° (5 mm), $n^{20}D$ 1.5132, d^{20}_4 1.0928, MR_D 57.85; calculated 60.77.

Found %: C 68.07; H 10.36; CH_3CO 20.89. $C_{12}H_{22}ON_2$. Calculated %: C 68.53; H 10.54; CH_3CO 20.47.

In a similar manner the hydrogenation of anabasine (I) gave α,β-bipiperidine (IV), which had b.p. 113–114° (5 mm) and m.p. 66–68°.

Saponification of N-acetyl-α,β-bipiperidine (III). One gram of monoacetylbipiperidine (III) was dissolved in 10 ml of water and 20 ml of concentrated hydrochloric acid. The mixture was boiled under reflux on the water bath. The solution after cooling was neutralized with concentrated alkali and the bipiperidine was extracted with ether. The ether was distilled off, and the residue was vacuum-distilled. B.p. 113–114° (5 mm), m.p. 66–68° (from ether). These constants are in good agreement with the literature data for bipiperidine.

Preparation of N,N'-diacetyl-α-β-bipiperidine (IV). One gram of monoacetylbipiperidine (III) was placed in a four-necked flask, fitted with reflux condenser, mechanical stirrer, gas inlet tube and thermometer, and then 10 ml of acetone, containing 0.1 ml of glacial acetic acid, was added. Ketene was bubbled into the reaction mixture for 10 minutes. The amount of acetone consumed in pyrolysis was 30 ml. Evolution of heat during reaction was not observed. Then the reaction products were transferred to a small Wurtz flask, and the acetone removed by distillation. The residue was vacuum-distilled. The fraction with b.p. 232–235° (5 mm) was collected; yield 0.8 g.

$n^{20}D$ 1.5322, d^{20}_4 1.1316, MR_D 68.85; calculated 70.35.

Found %: C 66.20; H 9.32. $C_{14}H_{24}O_2N_2$. Calculated %: C 66.63; H 9.52.

Acetylation of bipiperidine. One gram of bipiperidine with m.p. 66–68° was acetylated with ketene in a solution of 20 ml of acetone, containing 0.1 ml of glacial acetic acid. In heating the reaction mixture no noticeable change was observed. The amount of acetone consumed in pyrolysis was 60 ml. After reaction we isolated N,N'-α,β-bipiperidine with b.p. 232–235° (5 mm) and $n^{20}D$ 1.5322. Yield 0.7 g.

SUMMARY

1. The previously unknown monoacetyl- and diacetylbipiperidines were synthesized.

2. The position of the acetyl group in ammodendrine was determined.

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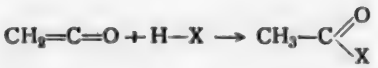
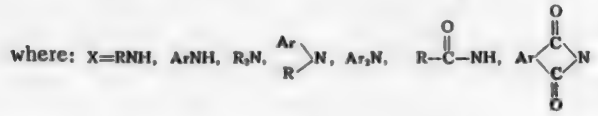
THE REACTION OF KETENE WITH NITROGEN-CONTAINING BASES

VI. THE MECHANISM OF THE ACETYLATION OF AMINES WITH KETENE

Iu. V. Svetkin

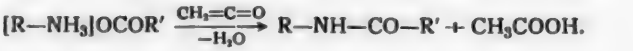
At the present time it is considered in the literature that the acetylation of amines by ketene proceeds in one stage by the equation





However, this hypothesis disagrees with experimental fact. As is known, in most cases the reaction of carbomethylene with various classes of organic compounds, including amines, is possible only in the presence of catalysts. In addition, a series of chemists have shown that ketene does not react directly with amines [1–6]. Finally, this treatment of the problem cannot be considered correct from purely theoretical considerations as it originates formally from general ideas on the ethylene bond.

In previous work we showed [3,7] that the acetylation of some amines with ketene in the presence of water proceeded through the formation of the corresponding acetates. Consequently, in this case also ketene does not react directly with amines (as in the examples given previously [1–7]) and thus the mechanism of this reaction remains unexplained at the present time. Therefore, if the formation of acetates as intermediates in the acetylation of amines were definitely established, it would be very valuable for determining the mechanism of this reaction. The secondary bases selected for this work were some which give salts with acetic acid that may be isolated readily in the form of stable crystalline substances. On the other hand, it is known that amines and acids in a 1 : 1 molecular ratio give the corresponding ammonium bases. We used this property to determine whether the ketone acted as a dehydrating agent in the second stage of the acetylation. Then when the ketene reacted with these onium compounds, one would expect the formation of the corresponding anilides by the scheme



Using a number of amine salts, it was shown that they reacted with ketene to give only aceto derivatives. It follows from this that the ketene does not act as a dehydrating agent in the second stage of the reaction.

On the other hand, there is the possibility that molecular dissociation of the quaternary ammonium compounds occurs in nonpolar solvents. In order to determine if the reaction proceeded through this stage, we made use of the properties of the mixed anhydride of formic and acetic acid, which may be used as a formylating agent [8–11]. Therefore, in the case of the acetylation of amine formates with ketene, one would expect the formation of the corresponding formyl derivative if this dissociation did occur.

$$[RNH_3]O-C\begin{matrix}O\\H\end{matrix} \rightleftarrows R-NH_2 + HCOOH$$

$$HCOOH + CH_2=C=O \rightarrow CH_3COOCOH$$

$$RNH_2 + CH_3COOCOH \rightarrow RNH-CH=O + CH_3COOH$$

However, when ketene was passed into a solution of these salts, the formyl derivative was not formed. Acetanilides were the sole reaction products. Thus, this course of the reaction may also be excluded.

Finally, it could be postulated that ketene reacted with amine acetates in nonpolar solvents through the hydrogen atom located at the nitrogen, which would give an acetate of the substituted amide type. Due to the sharp fall in the basicity constants, acid would be eliminated and the acetyl derivative formed.

$$[RNH_3]OCOCH_3 + CH_2=\overset{+}{C}=\overset{-}{O} \rightarrow [R-\overset{+}{N}H_2COCH_3]\overset{-}{O}OCCH_3$$

$$[\overset{+}{R}NH_2COCH_3]\overset{-}{O}OCCH_3 \rightarrow RNH-COCH_3 + CH_3COOH$$

When the amines were acetylated with ketene in the presence of water or other polar solvents, the acetates formed underwent the following dissociation.

$$[R-NH_3]OCOCH_3 \rightleftarrows [RNH_3]^+ + CH_3C\overset{-}{O}\overset{-}{O}$$

This indicated that ketene can react only with ions containing hydrogen.

$$[RNH_3]^+ + CH_2=\overset{+}{C}=\overset{-}{O} \rightleftarrows [RNH_2COCH_3]^+$$

$$[R-NH_2COCH_3]^+ + \overset{-}{O}OCCH_3 \rightleftarrows R-NH-COCH_3 + CH_3COOH$$

Thus the acetylation proceeds by an ionic type of chain mechanism, subject to the rules of acid catalysis.

EXPERIMENTAL

General acetylation method for secondary amines and salts. Into a four-necked flask, fitted with a mechanical stirrer, a reflux condenser, a thermometer and a gas inlet tube, was placed 60 ml of solvent and 5 g of amine. The calculated amount of water for an amine, water ratio of 1:1, was added. The contents of the flask were stirred for several minutes and then the introduction of ketene was begun. After 8–10 minutes, the separation of a voluminous precipitate was observed. Some of the crystals were removed, washed with anhydrous acetone and dried in a vacuum desiccator and their melting point determined to identify the acetates of the starting amines. The rest of the salt was acetylated with ketene until the acetates dissolved completely. After this the addition of ketene was stopped, the solvent partially distilled off and the melting points of the anilides precipitated were determined.

The acetylation of previously prepared salts was performed in dry solvents. The rest of the method was the same as the previous one. The acetylation of salts in water proceeded considerably faster. The amine salts which were not crystalline substances were prepared by mixing equimolar amounts of the amine and the appropriate acid in anhydrous solvents. The formylation was by the methods in [8–11]. In all cases we obtained appropriate amine derivatives, which agreed with the data of previous authors completely; therefore we do not present the results of this part of the work. The results of experiments on acetylation are listed in the table.

SUMMARY

A mechanism is proposed for the acetylation of amines by ketene in the presence of water or acids. This reaction obeys the usual rules of acid catalysis.

Expt. no.	Starting material		Added to amine (1 : 1)	Acetyl derivative		Yield (in %)
	formula	melting point		formula	melting point	
1	$(C_6H_5)(C_6H_{11})NH$	b.p. 139—141° (9mm)	H_2O	$(C_6H_5)(C_6H_{11})NCOCH_3$ *	68—69°	92
2	$[(C_6H_5)(C_6H_{11})NH_2]OOCCH_3$ . .	154	—	$(C_6H_5)(C_6H_{11})NCOCH_3$	the same	90
3	$[(C_6H_5)(C_6H_{11})NH_2]OOCC_3H_7$ . .	—	C_3H_7COOH	$(C_6H_5)(C_6H_{11})NCOCH_3$**	the same	92
4	$(C_6H_{11})_2NH$	b.p. 123—125° (17mm)	H_2O	$(C_6H_{11})_2NCOCH_3$*	102°	93
5	$[(C_6H_{11})_2NH_2]OOCCH_3$	64—65°	—	$(C_6H_{11})_2NCOCH_3$	the same	90
6	$[(C_6H_{11})_2NH_2]OOCC_3H_7$	—	C_3H_7COOH	$(C_6H_{11})_2NCOCH_3$**	the same	91
7	$(C_6H_5)(\alpha\text{-}C_{10}H_7)NH$	62	CH_3COOH	$(C_6H_5)(\alpha\text{-}C_{10}H_7)NCOCH_3$	115°	93
8	$(C_6H_5)(\beta\text{-}C_{10}H_7)NH$	108	CH_3COOH	$(C_6H_5)(\beta\text{-}C_{10}H_7)NCOCH_3$	93	92
9	$[\beta\text{-}C_{10}H_7NH_3]OOC_3H_7$	—	C_3H_7COOH	$(\beta\text{-}C_{10}H_7)NHCOCH_3$**	134	94
10	$(o\text{-}CH_3C_6H_4NH_3)OOCH$	61—64	—	$o\text{-}CH_3C_6H_4NHCOCH_3$***	110	95
11	$(o\text{-}CH_3C_6H_4NH_3)OOCCH_2Cl$ . .	95	—	$oCH_3C_6H_4NHCOCH_3$****	the same	94
12	$(o\text{-}CH_3C_6H_4NH_3)OOCC_3H_7$ . . .	—	C_3H_7COOH	$o\text{-}CH_3C_6H_4NHCOCH_3$**	the same	92
13	$(p\text{-}CH_3C_6H_4NH_3)OOCCH_2Cl$ . .	101	—	$p\text{-}CH_3C_6H_4NHCOCH_3$****	the same	83
14	$(p\text{-}CH_3C_6H_4NH_3)OOCC_6H_5$ . . .	52—53	—	$pCH_3C_6H_4NHCOCH_3$*****	the same	90

*Acetates were formed in the first stage of acetylation.

**The butyryl derivative was not found.

***The formyl derivative was not found.

****The chloroacetyl derivative was not found.

*****The benzoate was not found.

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A STUDY OF THE COMPARATIVE REACTIVITY OF THE HYDROXYL GROUPS IN CELLULOSE*

V. THE DISTRIBUTION OF METHOXY GROUPS IN PARTLY-METHYLATED CELLULOSE OBTAINED IN AN ALKALINE MEDIUM AT DIFFERENT CONCENTRATIONS OF ALKALI

V. Derevitskaia, M. Prokof'eva and Z. Rogovin

An earlier work [1] gave the results of a study of the reactivity of the hydroxyl groups in cellulose in the reaction involving the formation of alkali cellulose by treatment of the cellulose with 18% alkali and subsequent methylation. In the present work, alkali cellulose was prepared by treating cellulose with alkali solutions of different concentrations – 8, 13 and 40%. The alkali cellulose formed was pressed out until its weight was 3 times that of the original cellulose and washed free from adsorbed alkali using dry isobutyl alcohol. The washed alkali cellulose was methylated. In certain cases the alkali cellulose, pressed out to 3 times its weight, was methylated without being washed.

TABLE 1

Specimen No.	Alkali concentration (%)	Alkali cellulose composition, γ (from Na)	OCH_3 content (%)	γ for methylcellulose
1	8	46	4.7	26.3
2	8	48	4.8	27.0
3	8	49	4.1	23
4	13	101	15.5	87.5
5	13	105	16.9	91
6	13	98.5	14.8	87.5
7	13	95.5	—	—
8	40	100.9	16.0	90.8
9	40	94.2	15.6	88.7
10	40	108.7	18.6	105

Table 1 gives characteristic data for the washed alkali cellulose and corresponding methylcellulose specimens obtained.

It can be seen from the data given in Table 1 that as the alkali concentration is changed from 13 to 40%, the value of γ for the alkali cellulose remains unchanged and is equal to approximately 100. When the alkali cellulose is methylated, the methylcellulose obtained has a value for γ which is very close to the value of γ for the alkali cellulose. When the alkali concentration is reduced to 8%, the washed alkali cellulose has a lower value for γ, and when this is methylated, the methylcellulose obtained has a value for γ which is approximately one-half of the value of γ for the original alkali cellulose.

TABLE 2

Specimen no.	Alkali concentration (%)	OCH_3 content (%)	γ for methylcellulose
1	8	5.68	32.2
2	8	3.16	18
3	8	3.53	26
4	13	14	79
5	13	11.6	66.2
6	13	14.8	83.5
7	13	16.3	92
8	40	30.8	173
9	40	29.5	169
10	40	30.9	174

Unwashed alkali cellulose obtained by the action of 8–13% alkali, like that obtained by the action of 18% alkali [1], gives, on methylation, methylcellulose with values of γ (Table 2) which are very close to the values of γ for the methylcellulose obtained by methylation of the corresponding washed alkali celluloses.

When cellulose is treated with 40% alkali and the alkali cellulose obtained is subsequently methylated

* 64th communication in the series "A Study of the Structure and Properties of Cellulose".

without being washed, the methylcelluloses obtained have considerably higher values of γ than those for methylcelluloses obtained from washed alkali cellulose. The value of γ for this methylcellulose is much higher than the value of γ for all the other methylcelluloses given above. This indicates that the value of γ for alkali cellulose obtained by treating cellulose with 40% alkali is higher than the value of γ as determined by the direct method, in which the alkali cellulose is washed with alcohol, so that alcoholysis is unavoidable. It is known from data obtained by an indirect method that the quantity of combined alkali in alkali cellulose obtained by treatment with 40% alkali is ~2 times greater than the combined alkali content in alkali cellulose obtained by treatment with 13–18% alkali [2].

TABLE 3

Specimen no.	Alkali concentration (%)	γ for methylcellulose	Triphenylmethylcarbinol content in the methylcellulose trityl ether (%)	γ for methylcellulose trityl ether	No. of OCH_3-groups on 6tn C-atom	Z*
1	8	96.5	53.0	71.0	29.0	1.2
2	13	87.5	55.2	76.0	24.0	1.3
3	13	87.5	53.6	72.1	27.9	1.1
4	13	91.0	54.2	73.5	26.5	1.2
5	40	88.7	57.5	86.3	13.8	2.7
6	40	90.0	57.0	83.2	16.8	2.2
7	40	105.0	57.5	86.3	13.8	3.3

In order to study the distribution of methoxy groups in the chain unit of the methylcelluloses obtained, the number of free primary hydroxyl groups was determined by the tritylation method, and in a number of cases an additional method involving nitration with subsequent iodination was used. The results of the study of the methylcelluloses obtained from washed alkali cellulose are given in Table 3.

A study of the methylcelluloses obtained from unwashed alkali cellulose gave analogous results. Thus tritylation of methylcellulose with $\gamma = 92$ (Specimen 7, Table 2) yielded a trityl ether with $\gamma = 71.5$ and a corresponding value for $Z = 1.11$.

The data in Table 3 show that when the concentration of alkali is increased from 13 to 40% the value of Z increases sharply, i.e. as the alkali concentration is increased to 40% the process of alkali cellulose formation and subsequent methylation takes place more selectively.

TABLE 4

Specimen No.	γ for the methylcellulose	Total γ for the methylcellulose nitrate $\gamma OCH_3 + \gamma ONO_2$	γ for the methylcellulose iodonitrate γI
3, Table 3	87.5	286.5	72.5
6, Table 3	90.0	297.0	88.3

In a number of cases, in addition to the tritylation method, a method involving nitration of the methylcelluloses and subsequent iodination was used to determine the number of primary hydroxyl groups.

It can be seen from a comparison of the data in Tables 3 and 4 that the results obtained are in good agreement with those obtained by the tritylation method.

* Z – the ratio of the average number of methoxy groups attached to 1 secondary carbon atom to the number of methoxy groups attached to the primary carbon atom.

EXPERIMENTAL

Cotton was used as the starting material [1]. The alkali cellulose was prepared by treating the cellulose with an alkali solution of the required concentration (8, 13 and 40%) at 20° for 1 hour with a liquor ratio of 20 : 1, after which it was wrung out to 3 times its weight. The preparation of the washed alkali cellulose, the methylation of the alkali cellulose with methyl iodide, and the determination of the number of free primary hydroxyl groups by tritylation of the methylcelluloses or by iodination of the methylcellulose nitrates, were carried out as described earlier [1].

SUMMARY

1. A study has been made of the distribution of methoxy groups in partly-methylated cellulose obtained by the action of methyl iodide on alkali cellulose prepared in alkali with concentrations varying from 8 to 40%.

2. The distribution of methoxy groups in the methylcellulose changes as the concentration of the alkali used for the preparation of the alkali cellulose changes from 13 to 40%. The reaction involving alkali cellulose formation and subsequent methylation proceeds more selectively with the secondary hydroxyl groups at an alkali concentration of 40%.

3. When unwashed alkali cellulose, obtained by the action of 40% alkali solution, is methylated, the methylcellulose obtained has considerably higher values of γ (169-179) than the methylcelluloses obtained by methylation of the corresponding washed alkali cellulose (88-105). It is evident that the value of γ for this alkali cellulose is higher than the value of γ obtained by the direct method, in which alcoholysis of the alkali cellulose takes place.

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A STUDY OF THE COMPARATIVE REACTIVITY OF THE HYDROXYL GROUPS IN CELLULOSE*

VI. THE DISTRIBUTION OF METHOXY GROUPS IN THE PRODUCTS OF THE METHYLATION OF Na CELLULOSE ALCOHOLATE

V. Derevitskaia, M. Prokof'eva and Z. Rogovin

Sodium cellulose trialcoholate was first prepared by Scherer and Hussey [1], who treated cellulose with a solution of metallic sodium in liquid ammonia. They measured the volume and rate of evolution of hydrogen in this reaction and established that the amount of hydrogen corresponded to the formation of sodium cellulose trialcoholate, noting at the same time that one mole of hydrogen was liberated rapidly while the two others were liberated very slowly. The reaction between cellulose and metallic sodium in liquid ammonia was next studied by Shorygin and Makarova-Zemlianskaia [2]. They also obtained sodium cellulose trialcoholate, but did not observe a sharp difference in the rate of evolution of hydrogen throughout the reaction. The alcoholate obtained was methylated to yield methylcellulose with $\gamma = 100$. An attempt to determine the distribution of methoxy groups in the chain unit of the methylcellulose obtained, by methods involving tritylation and hydrolysis with subsequent separation of the osazones, was unsuccessful. Timmel [3] used the reaction involved in the formation of sodium cellulose alcoholate in liquid ammonia in his studies of the structure of cellulose. It can be seen from data given in this work on the measurement of the rate of evolution of hydrogen that the first mole of hydrogen is evolved at the highest rate.

TABLE 1

Specimen No.	Quantity of Na (in moles per mole of cellulose)	Time required for the evolution of the first mole of hydrogen τ_1 (seconds)	τ_1*: τ_2: τ_3
1	3	365	1:2.2:19
2	3	332	1:2.15:18.5
3	9	237	1:2.:16.7
4	1+1+1	1426	1:1.92:11.5

* τ_1 taken as unity.

Thus in spite of the fact that the reaction involved in the formation of sodium cellulose alcoholate in liquid ammonia has been studied by a number of workers, there are no data at present on the reactivity of the hydroxyl groups in cellulose in the reaction with metallic sodium. In the present work an attempt has been made to arrive at a solution to this problem.

The preparation of sodium cellulose alcoholate and the measurement of the rate of hydrogen evolution were carried out in the apparatus and using the method described by Shorygin and Makarova-Zemlianskaia [2]. The experiments were carried out on pulped cotton sulfite cellulose and on viscose rayon. Measurements were made of the time taken for the evolution of each mole of hydrogen in the reaction between cellulose and

* 65th communication in the series "A Study of the Structure and Properties of Cellulose".

sodium at different sodium concentrations. In some of the experiments the sodium was added at the start of the experiments in an amount corresponding to 3 moles per mole of cellulose or in large excess, while in other experiments the sodium was added in 3 separate portions. The rate of reaction varied with the amount of sodium added for reaction, but the ratio of the times required for the evolution of the first, second and third moles of hydrogen ($\tau_1 : \tau_2 : \tau_3$) remained practically constant (Tables 1, 2).

TABLE 2

Specimen No.	Quantity of Na (in moles per mole of cellulose)	Time required for the evolution of the first mole of hydrogen τ_1 (seconds)	τ_1 * : τ_2 : τ_3
1	3	155	1 : 1.6 : 7.8
2	9	125	1 : 1.68 : 7.55
3	9	144.5	1 : 1.57 : 7.6
4	1+1+1	512	1 : 1.71 : 8.1
5	1+1+1	539	1 : 1.64 : 7.05

* τ_1 taken as unity.

The total rate of reaction and the ratio $\tau_1 : \tau_2 : \tau_3$ depend on the nature of the cellulose specimen. The rate of evolution of the first mole of hydrogen in the reaction with metallic sodium in the case of viscose rayon (Table 1) exceeds the rate of evolution of the third mole by a factor of 16-18, whereas in the case of the pulped cellulose (Table 2) the factor is 7-8. This is evidently explained by the difference in the total reaction rates: the rate of formation of sodium cellulose trialcoholate in the reaction between sodium and cellulose pulp is 3-5 times greater than the rate of this reaction for viscose rayon. The influence of the total reaction rate on the ratio of the rates at which the three hydroxyl groups in cellulose react has been shown in a number of examples. Thus in the acetylation of cellulose [4] in the presence of catalysts, when the rate of reaction is high, the ratio of the reactivities of the primary and secondary hydroxyl groups in this reaction is 2.5 : 1, whereas at a low rate of acetylation without catalyst, this ratio is 16 : 1.

TABLE 3

Specimen No.	Starting material	γ for the sodium cellulose alcoholate	γ for the methyl-cellulose	γ for the methylcellulose trityl ether	Number of OCH_3--groups on the 6th C atom
1	Cotton	100	53	99	1
2	"	100	48	98.5	1.5
3	"	100	68	97	3
4	Viscose rayon	100	68	100	0
5	" "	100	50	102	0
6	" "	100	89	101	0
7	Cellulose pulp	100	102	95	5
8	" "	200	130	64	36
9	" "	200	131	67.8	32.2
10	" "	200	143	58	42

We have assumed that the considerable difference in the rates of evolution of the 3 moles of hydrogen in the reaction between cellulose and metallic sodium is determined chiefly by the different reactivities of the hydroxyl groups of cellulose in this reaction. In order to confirm this assumption, it was necessary to study the distribution of sodium in the chain unit of the sodium cellulose alcoholate. Since the direct study of sodium cellulose alcoholate is difficult due to its low stability, specimens of sodium cellulose alcoholate with $\gamma = 100 - 200$ were methylated and a study made of the distribution of methoxy groups in the methylcelluloses obtained. Before the methylation process, the ammonia was completely removed from the reaction medium by blowing dry nitrogen through it, and the sodium cellulose alcoholate was methylated with methyl iodide in the same

reaction vessel at room temperature for 12 hours. This yielded methylcellulose with a very low methoxy group content (1.6–2%). In subsequent experiments the ammonia was not removed completely or in some cases was extracted from the sodium cellulose alcoholate using dry toluene.

In order to obtain methylcellulose with a higher degree of methylation, some of the methylcellulose specimens were treated a second time with a solution of sodium in liquid ammonia and then with methyl iodide. This yielded methylcelluloses with $\gamma = 30-143$, in which the number of free primary hydroxyl groups was determined by the tritylation method. The results of the tritylation showed (Table 3) that the formation of sodium cellulose alcoholate with γ up to ≈ 100 and subsequent methylation take place exclusively with the secondary hydroxyl groups. In the methylcellulose with $\gamma \approx 100$, practically all the primary hydroxyl groups are free.

Further reaction involving the formation of sodium cellulose alcoholate with $\gamma > 100$ takes place with the primary hydroxyl groups.

The data obtained on the distribution of methoxy groups in the products of the methylation of sodium cellulose alcoholate confirm the assumption made above, that the difference in the rates of evolution of the 3 moles of hydrogen in the reaction involved in the formation of sodium cellulose alcoholate is caused chiefly by the difference in the affinities of the three hydroxyl groups toward sodium.

EXPERIMENTAL

The starting materials used were scoured cotton [5], viscose rayon and pulped sulfite cellulose [5].

The sodium cellulose alcoholate was prepared by treating the cellulose with a solution of metallic sodium in liquid ammonia in the apparatus and using the method described in [2]. The ammonia was dried thoroughly and redistilled twice. No hydrogen was evolved when the metallic sodium was added, indicating that no moisture was present. The sodium was introduced into the reaction vessel either all at once at the start of the reaction or in portions at separate stages of the reaction. The hydrogen liberated was collected in a eudiometer over acidified water. The end of the reaction was established from the disappearance of the characteristic blue color of the solution of sodium in ammonia and the end of the hydrogen liberation. The time required for the liberation of each milliliter of hydrogen was measured using a stopwatch, in order to determine the rate of hydrogen evolution. The sodium cellulose alcoholate was methylated using sodium iodide (26–35 moles per mole of the alcoholate) in the same apparatus at room temperature for 12 hours. Before the methylation, the ammonia was evaporated from the reaction vessel until the sodium cellulose alcoholate was only slightly wet with ammonia, after which the methyl iodide was added. In some cases the ammonia was extracted from the sodium cellulose alcoholate using toluene. The methylation products were washed with hot and then with cold methanol and acetone, dried and analyzed.

The methods used for the determination of the methoxy group content, the tritylation of the methylcellulose and the analysis of the trityl ether have been described earlier [5].

SUMMARY

1. A study has been made of the distribution of methoxy groups in partly-methylated cellulose obtained from sodium cellulose alcoholate.

2. The formation of sodium cellulose alcoholate with γ up to 100 and subsequent methylation take place only with the secondary hydroxyl groups of the cellulose; further reaction involving the formation of sodium cellulose alcoholate with $\gamma > 100$, and methylation of the product, proceeds with the primary hydroxyl group of the cellulose.

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THE KINETICS OF OXIDATION OF CELLULOSE BY NITROGEN PEROXIDE ACCORDING TO DATA OBTAINED FROM THE ABSORPTION SPECTRA OF THE PRODUCTS

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The product of oxidation of cellulose by nitrogen peroxide possesses a number of valuable properties: good solubility in alkali, the ability to form insoluble salts with polyvalent metals, etc. It is recommended for use in medicine for various purposes [1–4]. This product was obtained by Shorygin and Rogovin and their co-workers [6], while studying the nitration reaction. Its properties have been studied by a number of authors [6–10, 12, 15, 24, 25]. The reaction mechanism of the oxidation of cellulose by nitrogen peroxide has been investigated by McGee and co-workers [11], Nabar and Padmanabhan [16], etc.

In spite of a large amount of work connected with the oxidation of cellulose by nitrogen peroxide the kinetics of this reaction has been studied very inadequately and the hypotheses put forward on the mechanism of the process have not been substantiated [13]. The application of new, particularly spectroscopic, methods has enabled us to establish a number of new and very interesting facts connected with the mechanism of the reaction. On the basis of an investigation of the spectra of organic nitrites, their solutions, the oxides of nitrogen in the free and adsorbed states, nitric and nitrous acids, oxidized cellulose before and after pumping out the samples under vacuum, heating and treating with solvents, we have shown that among the macromolecular products from the oxidation of cellulose with NO_2, in addition to substances containing carboxyl and carbonyl groups, a considerable quantity of cellulose nitrite occurs [5]. For the determination of its content in the oxidation products we used the magnitude of the optical density at λ 365 mμ; the carboxyl group was determined by the change in the optical density at λ 250 mμ, and the carbonyl group at λ 280 mμ [5, 19].

EXPERIMENTAL

Samples of cellophane were oxidized by nitrogen peroxide at 31° for periods of 10, 20, 45, 140, 180, 285 and 450 minutes in a specially constructed apparatus, using a method developed by us. A detailed description of the method has already been published [20].

Results of the spectrophotometric study of the samples obtained, in the region 270–400 mμ, are given in Fig. 1.

As we have shown [5], the absorption in this region indicated the formation of nitrite. The intensity of the absorption band changes with time, denoting a change in the cellulose nitrite content. The thickness of the films was measured by means of a vertical IZV-1 gauge. The cellophane used had a thickness of 29.7 μ. Assuming that the optical density of a layer of constant thickness for the same wave line (365 mμ) is proportional to the nitrite content, we constructed a graph of the variation of optical density, and hence also of the nitrite content, with time of oxidation. The nitrite content grows initially, then a maximum is reached after 45 minutes at 25°, after which it falls to a constant value.

Films of oxidized cellophane, after washing with water and drying, were re-examined spectrophotometrically. The absorption bands characteristic of nitrites then disappeared completely. This would explain the results of Rowen et al. [18] who examined the absorption spectra of samples oxidized with NO_2 only after treatment with water, no nitrite absorption bands being observed. The spectra of water-washed products, in the region 210–270 mμ,

are given in Fig. 2. An intense absorption maximum is seen at about 220 mμ. A small absorption band at 280 mμ is seen in Fig. 4. As we have discussed previously [5, 19], the presence of the absorption maxima at 220 and 280 mμ is connected with the presence of carboxyl and carbonyl groups in the product. The carboxyl group content was also determined by the calcium acetate method and the carbonyl group content by the hydroxylamine method [29]. The quantity of carbonyl groups in the reaction products was 1–1.5%. The change in carboxyl and carbonyl group content, and also the equivalent weight of the product, can be estimated from the absorption curves as is done for many organic substances [21]. It is sufficient for our purpose to know the relative change in carbonyl group content during the course of the reaction. In this case the spectroscopic method gives very accurate and reliable results. For the determination of the absolute value of the carboxyl group content by the spectroscopic method, it is necessary to determine the carboxyl content of at least one sample by chemical methods. The curves of variation of optical density D, at λ 220 mμ, with time of oxidation have the same form as the curves of variation of carboxyl content with reaction time, obtained by the calcium acetate method. A carboxyl group content of about 19% corresponds to about 1.5 carboxyls to 2 elementary cellulose-chain segments. The limiting carboxyl content is reached in less than 500 minutes oxidation.

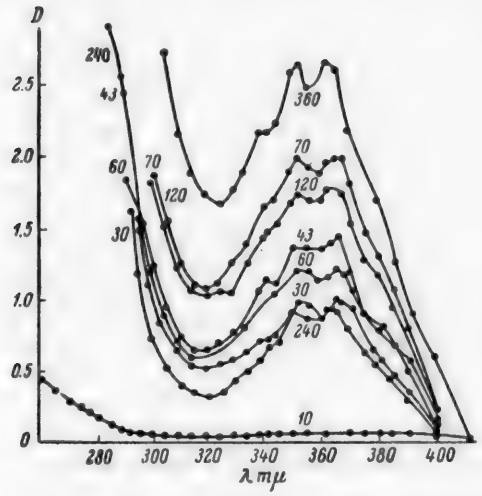

Fig. 1. Absorption spectra of cellulose films oxidized by nitrogen peroxide at 31°. [Reaction times (in minutes) shown on diagram on the corresponding curves.]

A study of the effect of temperature on the rate and mechanism of the oxidation reaction is of interest, both from the practical and theoretical points of view. We carried out a series of experiments on the oxidation of cellulose at 25, 31, 44 and 65°. In each series the samples were oxidized for a different time. The absorption curves from the experiments carried out at 25 and 44° had the same form as the curves of Fig. 1; however at higher temperature the separate maxima in the region 320–400 mμ became less sharp and the total absorption decreased. At long oxidation times a slight shift in the separate absorption maxima in the short wave region was observed.

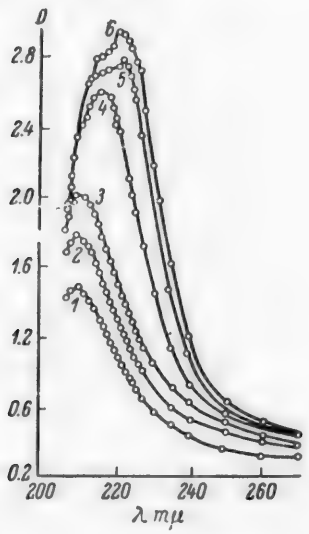

Fig. 2. Absorption spectra of products of oxidation of cellulose at 25°, obtained after treating the products with water and drying. Reaction time (in minutes): 1) 2, 2) 15, 3) 60, 4) 120, 5) 207, 6) 300.

Determination of the combined nitrogen content in our samples, by the Kjeldahl method, showed that the curves of variation of combined nitrogen with time, have the same form as those for the change in nitrite content. This is in conformity with our views on the large role of cellulose nitrite in the oxidation. A considerable proportion of combined nitrogen in the product corresponds to nitrite, and not to nitrate as a number of investigators assume. For the lower alcohols the formation of nitrites by the action of nitrogen peroxide, both in the vapor and liquid phases, has been established [27]. Fig. 3 shows curves of the variation of optical density D at λ 365 mμ with oxidation time, at 25, 31, 44 and 65°. From comparison of these curves with one another it is seen that the nitrite content falls with increasing

temperature and the time interval from the beginning of the experiment to the attainment of the maximum increases: at 25° after 45 minutes, at 31° after 70 minutes and at 44° after 180 minutes. While the maximum nitrite content depends on the temperature, its limiting content (at long reaction times) is approximately the same at the different temperatures. Oxidation of cellulose for 242 minutes at 65° gives no maximum in the optical density–reaction time curve.

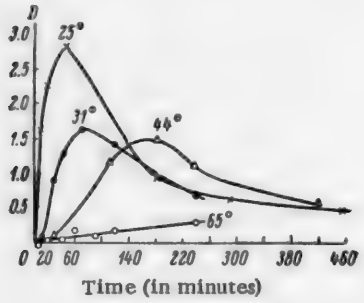

Fig. 3. Variation of optical density of films at λ 365 mμ with time of oxidation at 25, 31, 44 and 65°. (Temperature of experiments shown on the corresponding curves.)

The cellulose, oxidized for various times at different temperatures was kept for 24 hours in water vapor. After drying, the samples were examined spectroscopically. The results of one of these experiments, carried out at 44°, are given in Fig. 4.

At temperatures of 16, 25 and 31° the optical density at λ 250 mμ increases continuously during the course of oxidation, whereas at 44 and 65°, after reaching a maximum value, it decreases to some extent. The curves of variation of carboxyl group content at various temperatures, from the data of chemical analysis, have the same form. The product of 90 minutes oxidation at 65° contains 0.13 g-equiv. of COOH per 100 g of cellulose; on further oxidation the carboxyl content decreases a little. The product of 242 minutes oxidation at the same temperature still contains 0.12 g-equiv. of COOH per 100 g of cellulose. In the case of oxidation at lower temperatures (16, 25 and 31°) no lowering of carboxyl group content is observed after the attainment of a certain limiting value. Oxidation at 25° for 280 minutes gives a product containing up to 0.18 g-equiv. of COOH per 100 g of cellulose, and at 31° for 240 minutes–up to 0.23 g-equiv. The initial rate of formation of carboxyl groups increases with temperature. Thus, for example, a content of 0.08 g-equiv. of COOH per 100 g of cellulose is reached on oxidation at 65° in 15 minutes, at 44° in 27 minutes, at 31° in 36 minutes and at 16° in 70 minutes. One of the possible causes of the decrease in carboxyl group content in experiments at high temperatures, after attainment of the maximum content, could be decarboxylation, which in a strongly acidic medium in the presence of excess NO_2 takes place at a lower temperature than in dilute acids. It is known that oxidized cellulose undergoes rapid decarboxylation, going to completion after 6 hours boiling in 12% HCl, this frequently being used for determination of carboxyl groups in uronic acids.

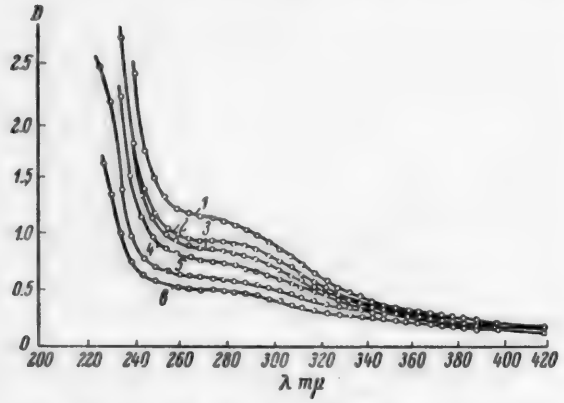

Fig. 4. Absorption spectra of cellulose films, oxidized at 44°, after treating samples with water for 24 hours and drying. Reaction time (in minutes): 1) 180, 2) 238, 3) 113, 4) 418, 5) 26, 6) 8.

An increase in the oxidation temperature can favor an increase in the intra- and intermolecular interaction of carboxyl and hydroxyl groups. Kaverzneva [17] has pointed out that ester and lactone groups are formed on oxidation of cellulose. Besides the chemical method, the lactone group can also be detected by the spectroscopic method [28].

DISCUSSION OF RESULTS

The reaction, which proceeds with the formation of an intermediate product, can be represented by the following scheme: $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. The simplest case of a stepwise reaction was considered by Radovskii [22].

His equations enable us to explain the mechanism observed by us in the oxidation of cellulose by NO_2. The initial product in our case is cellulose: the intermediate—cellulose nitrite, and the end product—monocarboxycellulose. Figure 5 gives curves of change of nitrite content (Curve 1) and carboxyl (Curve 2) with time of oxidation at 31°. As is seen from the graph, the variation of nitrite content with time has all the characteristics of a curve of variation of content of an intermediate product B in a stepwise reaction of the type $A \rightarrow B \rightarrow C$. The accumulation of carboxyl groups in this case is analogous to the accumulation of the end product C. Stepukhovich and Bakhareva [23], in an analysis of the kinetics of stepwise reactions, established that the time of maximum accumulation of intermediate product coincides with the time corresponding to the point of inflection on the curve of accumulation of end product only in the case where the transformations of A to B and of B to C are of the same order. Hence in our case we can assume that the two consecutive reactions are reactions of the same order. Curve 1 of Fig. 5, in fact, passes through a maximum corresponding to the time of the point of inflection that is observed in Curve 2 for the formation of the end product; Curve 2 (Fig. 5) is characterized by an initial rate increase, which also should occur in a stepwise reaction. Note that the similar S-shaped form of the curve of carboxyl group content also agrees with the data [24, 25]. The curve in Fig. 6 shows the variation of rate of formation of carboxyl groups with time.

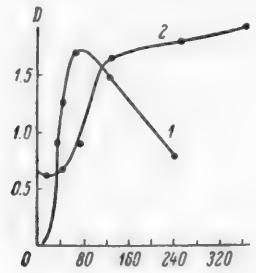

Fig. 5. Change in quantity of nitrite (1) and content of carboxyl groups (2), with time of oxidation at 31°, from absorption spectra data.

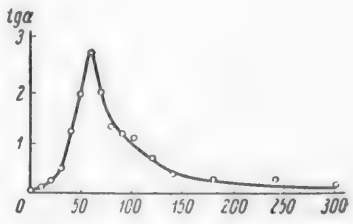

Fig. 6. Change in the relative rate of formation of carboxyl groups with time of oxidation of cellulose by nitrogen peroxide at 31°.

The described relationships of the change of nitrite and carboxyl group contents allow the assumption to be made that the formation of monocarboxycellulose in our experiments proceeds through the formation of cellulose nitrite. Our experimental data and the conclusions drawn from them are in good agreement with the data of a number of other authors, which show that the oxidation of low-molecular alcohols by nitrogen peroxide proceeds through the formation of nitrites [30].

Our data provide a ready explanation also for the acceleration of the reaction on introduction of HNO_3, observed by McGee et al. [11]. Nitric acid reacts with NO_2, forming HNO_2 which esterifies the cellulose simultaneously with the HNO_3 and, by reacting with N_2O_3, regenerates NO_2. From the experiments of Pigman [14] and of Zverev [3], it can be concluded that under conditions which bring about the formation of HNO_2, the reaction will be accelerated. However in their papers the mechanism of the action of HNO_2 is not made clear. It should be particularly noted that with the action of HNO_3, oxidation is considerably accelerated by the addition of $NaNO_2$, which evolves HNO_2, and that on addition of urea, which combines with HNO_2, the reaction is strongly retarded. In all these cases an excess of water retards the reaction and an increase in the $NaNO_2$ content accelerates it. Excess water hinders the formation of cellulose nitrite or assists its hydrolysis.

Let us now turn to Fig. 3 which shows the variation of nitrite content with time of oxidation at different temperatures. On raising the temperature the magnitude of the maximum decreases but the time required for its attainment increases. This implies that in conformity with the analysis of the characteristics of stepwise reactions, at high temperatures the ratio of the rate constant of formation of nitrite to the rate constant of formation of carboxyls decreases.

$$\left(\frac{k_1}{k_2}\right)_{25°} > \left(\frac{k_1}{k_2}\right)_{31°} > \left(\frac{k_1}{k_2}\right)_{44°}$$

The time for the attainment of the maximum nitrite content at 25° is 45 minutes, at 31°, 70 minutes and at 44°, 180 minutes. The quantities of nitrite in the maxima at 25, 31 and 44° are in the ratio 3 : 1.95 : 1.55. It would be interesting to examine how the decrease in the ratio $\frac{k_1}{k_2}$ at high temperatures is related to the change in the rate constants of formation of nitrite and carboxyls in these circumstances.

The curves of Fig. 3 also have another characteristic feature. On increasing the temperature the development of an induction period in the formation of nitrite appears. Possibily at high temperatures the stepwise reaction is complicated by the formation of new intermediate products, prior to the nitrite.

By making use of Fig. 2 we found, by a graphical method, the apparent initial rate of formation of nitrite $\frac{d(x-y)}{dt}$ at different temperatures; this value decreases with increasing temperature. At the same time there is a decrease in the content of the dimer N_2O_4 with increasing temperature as a result of dissociation. Hence it can be assumed that the active agent in the oxidation of cellulose is the dimer N_2O_4. This is not in agreement with Nevell's conclusion, which he drew by analogy with the action of nitric acid, that the active oxidizing agent is the monomer NO_2. We have established that the ratio of the rate constant of formation of nitrite to that of formation of carboxyls decreases with increasing temperature. This decrease could be brought about both by a decrease in the rate constant of formation of nitrite and by an increase in the rate constant of oxidation of nitrite with increase of temperature.

Schmid and Maschka [26] oxidized cyclohexanone and tetrahydrofuran with nitrogen tetroxide at different temperatures, and also in the presence of HNO_3 and HNO_2 at different concentrations. From the fact that the reaction is markedly accelerated by the simultaneous presence of HNO_3 and HNO_2, these authors concluded that the active oxidizing agent is nitrogen tetroxide.

SUMMARY

1. The cellulose nitrite content of the product previously obtained by us by the oxidation of cellulose with nitrogen peroxide has been studied spectroscopically.

It is shown that the quantity of nitrite passes through a maximum with time of oxidation. The maximum quantity of nitrite corresponds to the maximum rate of accumulation of carboxyl groups.

2. An investigation of the variation of the nature of the course of the reaction with temperature has been carried out. With increasing temperature the content of carboxyl groups decreases and also the quantity of nitrite. The maximum in the nitrite-content curve shifts with increasing temperature toward long reaction times and at 65° it no longer appears. This confirms that cellulose nitrite, detected by us, is an intermediate product in the oxidation of cellulose by nitrogen peroxide.

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SYNTHESIS OF HETEROORGANIC COMPOUNDS OF THE ALIPHATIC SERIES BY THE DIAZO METHOD

VIII. SYNTHESIS OF COMPOUNDS OF GROUP V ELEMENTS. ORGANOPHOSPHORUS COMPOUNDS. EXPERIMENTS ON THE SYNTHESIS OF DI- AND TRIHALOALKYL-PHOSPHINES AND SOME REACTIONS OF CHLOROALKYL DERIVATIVES OF PHOSPHORUS

V. A. Ginsburg and A. Ia. Iakubovich

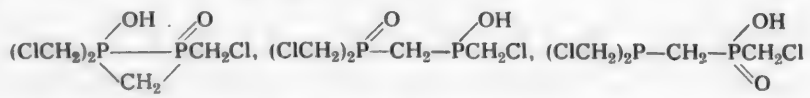
In attempts to extend our diazo method of synthesizing organophosphorus compounds of the aliphatic series [1] to the preparation of secondary and tertiary alkylphosphines by the scheme

$$RCHClPCl_2 \xrightarrow{RCHN_2} (RCHCl)_2PCl \xrightarrow{RCHN_2} (RCHCl)_3P$$

it was established that chloromethyldichlorophosphine and α-chloroethyldichlorophosphine react with diazomethane but under the conditions studied the expected di- and tri-(chloroalkyl)-phosphines were not formed. Instead of them we obtained organophosphorus compounds with a complex structure and a series of properties similar to those of the solid by-products formed by reacting aliphatic diazo compounds with phosphorus trichloride and tribromide. Apparently, the formation of this type of substance was also observed by Plets [2] who had tried unsuccessfully before us to prepare alkylphosphines by reacting diazomethane with phosphorus trichloride.

Chloromethyldichlorophosphine reacted with diazomethane in an ether solution to give a homogeneous, amorphous precipitate that did not distill or recrystallize and did not form any crystallizable derivatives. This made it difficult to isolate it in an analytically pure form. The data from elementary analysis of a series of preparations obtained in various experiments and the value of the molecular weight (found cryoscopically and as the gram-equivalent of a monobasic acid when the substance was titrated with sodium hydroxide in the presence of phenolphthalein) indicated the following empirical composition for the substance: $C_4H_9P_2Cl_3O_2$.

In order to determine the structure of the compound being examined the substance was decomposed with phosphorus pentachloride and also chlorinated with elementary chlorine. In the first case special treatment of the reaction products gave tri-(trichloromethyl)-phosphorus dichloride $(CCl_3)_3PCl_2$ and di-(chloromethyl)-phosphinic and phosphoric acids (in the form of aniline salts). The results obtained indicated that the compound being investigated has one of the following possible formulas, which include groups of atoms that were established experimentally $(\equiv C)_3P$, $(\equiv C)_2P$ and $(\equiv C)-P$.



In any case diazomethane reacted with chloromethyldichlorophosphine to give undoubtedly new phosphorus-carbon bonds and new chloromethyl groups, connected to phosphorus.

The formation of diphosphorus derivatives containing phosphorus atoms connected by a methylene group, may occur in this reaction either as a result of two phosphorus-containing molecules being connected by a methylene radical, formed during the decomposition of diazomethane, or due to alkylation of the chloromethyl-phosphine derivative by another molecule, containing trivalent phosphorus, for example by the scheme

$$(ClCH_2)_2PCl + ClCH_2PCl_2 \longrightarrow (ClCH_2)_2PCl_2{-}CH_2PCl_2$$

The occurrence of the latter reactions depends on the lability of the chlorine in the chloromethyl group, connected to phosphorus. To get an idea of the probability of such reactions occurring, we studied the reaction of the diethyl ester of chloromethylphosphinic acid with triethyl phosphite. It was found that the diethyl ester of chloromethylphosphinic acid reacted with triethyl phosphite only under drastic conditions and, in accordance with A. E. Arbuzev's scheme, ethyl chloride and the tetraethyl ester of methylenediphosphinic acid were formed. In addition to these substances considerable amounts of the diethyl ester of ethylphosphinic acid were always present in the reaction products and apparently were formed as a result of the side reaction of triethyl phosphite "isomerization" under the effect of ethyl chloride.

$$P(OC_2H_5)_3 + ClCH_2PO(OC_2H_5)_2 \longrightarrow (C_2H_5O)_2P(O)CH_2PO(OC_2H_5)_2 + C_2H_5Cl$$

$$P(OC_2H_5)_3 \xrightarrow{C_2H_5Cl} C_2H_5PO(OC_2H_5)_2$$

In contrast to the ester of chloromethylphosphinic acid, the diethyl ester of dichloromethylphosphinic acid did not undergo a similar reaction. The lability of a chlorine atom in a carbon chain in a position β to phosphorus was evaluated in a similar reaction, using the diethyl ester of β-chloroethylphosphinic acid and triethyl phosphite as examples, for a qualitative comparison. In this case the reaction, which gave the tetraethyl ester of ethylenediphosphinic acid, proceeded somewhat more readily and less by-product—the diethyl ester of ethylphosphinic acid—was formed.

$$P(OC_2H_5)_3 + ClCH_2CH_2PO(OC_2H_5)_2 \longrightarrow (C_2H_5O)_2P(O)CH_2CH_2PO(OC_2H_5)_2$$

Consequently, the chlorine atom was not very labile in α- and β-haloalkyl derivatives of pentavalent phosphorus (in acid esters) and drastic conditions were required for the formation of diphosphorus derivatives. The lability of the chlorine atom remained the same in the alkylation of phosphorus on going to chloromethyl derivatives of silanes, such as trialkoxychloromethylsilane and even quaternary chloromethyltrimethylsilane, with a less electronegative central atom, silicon. These silanes are quite similar to the previously unknown chloromethyldialkoxy- and chloromethyldialkylphosphines, in which the lability of the chlorine atom should be higher than in the derivatives of pentavalent phosphorus due to the smaller electrophilicity of P^{III}. In fact, chloromethyltrimethylsilane and chloromethyltriethoxysilane react more readily with triethyl phosphite than do chloromethylphosphine derivatives but this reaction, nevertheless, proceeds more readily at about 150° to form silylmethyl phosphine compounds that have not been described previously.

$$P(OC_2H_5)_3 + ClCH_2Si(CH_3)_3 \longrightarrow (C_2H_5O)_2P(O)CH_2Si(CH_3)_3$$

$$P(OC_2H_5)_3 + ClCH_2Si(OC_2H_5)_3 \longrightarrow (C_2H_5O)_2P(O)CH_2Si(OC_2H_5)_3$$

Thus, the formation of diphosphorus derivatives, containing the $P{-}CH_2{-}P$ group of atoms, by a reaction of diazomethane with chloromethyldichlorophosphine (under mild conditions) similar to the formation of phosphonium compounds, is improbable as is shown by the qualitative characteristics given above for the lability of chlorine in a chloromethyl group at a phosphorus atom in the alkylation of trivalent phosphorus compounds and also because of the lower basicity of the phosphorus atom in chloromethylchlorophosphines.

In characterizing tri-(trichloromethyl)-phosphorus dichloride, which we isolated by treating the reaction product of chloromethyldichlorophosphine and diazomethane described above with phosphorus pentachloride, we found that some of its properties are of general interest. This substance was also prepared by heating tri-(chloromethyl)-phosphorus oxide with phosphorus pentachloride.

$$(ClCH_2)_3PO \xrightarrow{PCl_5} (CCl_3)_3PCl_2$$

These observations indicate the particularly ready conversion of chloromethyl groups, connected to phosphorus, into trichloromethyl groups, as we had noted previously [3]. Tri-(trichloromethyl)-phosphorus dichloride is extremely stable to hydrolysis and when treated with boiling water it loses only one of the chlorine atoms connected to the phosphorus.

$$(CCl_3)_3PCl_2 \xrightarrow{H_2O} (CCl_3)_3P(OH)Cl$$

When treated with aniline the tri-(trichloromethyl)-phosphorus hydroxychloride thus obtained lost its acid halide chlorine and was converted to tri-(trichloromethyl)-phosphorus oxide.

$$(CCl_3)_3P(OH)Cl \xrightarrow{C_6H_5NH_2} C_6H_5NH_2 \cdot HCl + (CCl_3)_3PO$$

It seemed interesting to determine whether the stability of the P—Cl bond to hydrolysis we observed in trichloromethylphosphine compounds was maintained in the series of trivalent phosphorus compounds. For this we investigated trichloromethyldichlorophosphine, prepared by reducing trichloromethylphosphorus tetrachloride with yellow phosphorus in the presence of catalytic amounts of phosphorus triiodide.

$$CCl_3PCl_4 \xrightarrow[PI_3]{P} CCl_3PCl_2$$

It was found that when treated with water, trichloromethyldichlorophosphine (low-melting crystals, which were oxidized when heated in air to trichloromethylphosphinyl dichloride) was readily hydrolyzed and in addition to breaking of the P—Cl bond, hydrolytic cleavage of the C—P bond of the molecule occurred and gave phosphorus acid and chloroform. Thus, here the bond between the trichloromethyl group and trivalent phosphorus was found to have a tendency for haloform decomposition to an even greater extent than in the ester of trichloromethylphosphinic acid [4]. Hasseldine et al. [5] noted a similar readiness for hydrolysis of the CF_3—E bond in a series of P, As, Se and S compounds.

EXPERIMENTAL

1. Reaction of diazomethane with chloromethyldichlorophosphine. Preparation of the compound $C_4H_9P_2Cl_3O_2$. With vigorous stirring and cooling to -60°, a solution of 10 g of diazomethane in 300 ml of ether (dried over solid potassium hydroxide) was added dropwise to a solution of 20 g of chloromethyldichlorophosphine in 50 ml of dry ether. The reaction began immediately and was accompanied by the quantitative evolution of nitrogen (about 5 liters) and the formation of a white, curdy precipitate. As soon as the diazomethane decomposition slowed down and the reaction solution acquired a slowly disappearing yellow color, the temperature of the reaction mixture was raised to room temperature and the precipitate filtered off and washed carefully with dry ether. Evaporation of the ether in vacuum yielded 12.5 g of a substance which was readily soluble in water. Evaporation of the water in vacuum gave a hygroscopic glassy mass. Different samples of the substance were analyzed before and after hydrolysis and this gave values which agreed closely and from these, average values from the analysis data of five different samples were obtained.

Found %: C 18.85; H 3.24; Cl_{total}. 41.32; P_{total}. 23.97; P^{III}* 12.00. M (in acetic acid and acetophenone) 260; g-equiv. (using phenolphthalein) 256. $C_4H_9P_2Cl_3O_2$. Calculated %: C 18.6; H 3.5; Cl_{total}. 41.3; P_{total}. 24.0; P^{III} (for 1 atom) 12.00. M 257.5; g-equiv. for a monobasic acid 257.5.

The filtrate, remaining after removal of the precipitate, was evaporated in vacuum. There remained 8 g of a viscous, tar-like liquid, which decomposed during distillation.

2. Reaction of $C_4H_9P_2Cl_3O_2$ with phosphorus pentachloride. Preparation of tri-(trichloromethyl)-phosphorus dichloride. 5 g of the substance was heated for 90 minutes with 60 g of PCl_5 on a boiling water bath until it dissolved completely and then the reaction mixture was cooled (on cooling, the mixture crystallized) and sulfur dioxide passed into it. During this treatment the solid mass became liquid. The $POCl_3$ and $SOCl_2$ formed were carefully distilled off in vacuum at 30°. The crystals deposited were separated (2.5 g) to leave the filtrate as a thick, brown liquid (7.0 g). After recrystallization from petroleum ether, the crystals formed fine, colorless prisms with m.p. 190° (with decomp.), which contained hydrolyzable chlorine.

Found %: $Cl^{**}_{hydr.}$ 15.58. M 443. $(CCl_3)_3PCl_2$. Calculated %: $Cl_{hydr.}$ 15.52. M 457.5.

*A sample of the order of 0.2 g in 50 ml of 5% aqueous $NaHCO_3$ solution and 50 ml of 0.1 N I_2 was kept in the dark for 4 hours. Then the sample was acidified with 40 ml of 20% H_2SO_4 and the excess I_2 titrated with 0.1 N $Na_2S_2O_3$.

**A sample was dissolved in 10 ml of benzene and kept for 24 hours with 5 ml of aniline. The solution was diluted with water and the chlorine determined argentometrically.

3. Preparation of tri-(trichloromethyl)-phosphorus hydroxychloride. 1 g of tri-(trichloromethyl)-phosphorus dichloride was boiled for 30 minutes with 10 ml of water, after which the filtrate was sucked off and the crystals dried in vacuum and recrystallized from petroleum ether. We obtained 0.8 g of a substance with m.p. 203° (with decomp.). Further boiling of the substance with water or aqueous alkali did not produce ionic chlorine.

Found %: C 8.09, 7.91; H 1.01, 0.72; $H_{act.}$ 0.219, 0.274; Cl_{total} 80.70, 81.10. M 432. $(CCl_3)_3P(OH)Cl$. Calculated %: C 8.20; H 0.228; $H_{act.}$ 0.22; Cl 80.87. M 439.

4. Preparation of tri-(trichloromethyl)-phosphorus oxide. 2 g of $(CCl_3)_3P(OH)Cl$ was dissolved in 60 ml of benzene and 3.0 g of aniline added to the solution. After 1 day 0.58 g of aniline hydrochloride had precipitated. After being washed with 5% aqueous hydrochloric acid, the benzene solution was dried over sodium sulfate; the benzene was removed in vacuum. We obtained 1.2 g of tri-(trichloromethyl)-phosphorus oxide, which melted at +55° after recrystallization from methanol (with cooling to -70°). It was insoluble in water and aqueous alkali.

Found %: Cl 79.91, 79.30. M 412. $(CCl_3)_3PO$. Calculated %: Cl 79.38. M 402.5.

5. Hydrolysis of the liquid products formed during phosphorus pentachloride treatment of the compound $C_4H_9P_2Cl_3O_2$. The liquid filtrate remaining after separation of tri-(trichloromethyl)-phosphorus dichloride (see Experiment 2) was hydrolyzed and the mixture of acids formed resolved via aniline salts. 4.5 g of the liquid was treated with 30 ml of water for 3 days at room temperature. When the substance had dissolved, the water was removed in vacuum with a bath temperature of 30°. The residue was dissolved in 200 ml of amyl alcohol and 5 ml of aniline added. The precipitate of aniline salts was filtered off and recrystallized several times. We isolated 4.5 g of plate-like crystals with m.p. 180° and 0.5 g of thin needles, which were readily soluble in alcohol and reprecipitated from it by the addition of 50 volumes of benzene (m.p. 185–190° with decomp.).

Found %: C 37.84, 37.93; H 4.91, 3.99; Cl 27.08, 27.81; N 6.34, 6.07. $(ClCH_2)_2POOH \cdot C_6H_5NH_2$. Calculated %: C 37.50; H 4.70; Cl 27.37; N 5.45.

The plate-like crystals were aniline phosphate.

Found %: C 49.39, 48.87; H 6.43, 6.33; N 10.07, 9.88. $H_3PO_4 \cdot 2C_6H_5NH_2$. Calculated %: C 50.70; H 5.98; N 9.85.

6. Action of chlorine on the compound $C_4H_9P_2Cl_3O_2$. 5 ml of CCl_4 was poured onto 5 g of the substance, which was chlorinated with elementary chlorine at 50° for 3 days. The bulk of the substance was converted into a product which was viscous when heated and friable in the cold. 4 g of the substance obtained was dissolved in 10 ml of water and the excess water removed in vacuum at room temperature. The sirupy residue was dissolved in amyl alcohol; the solution was then treated with 5 ml of aniline. The precipitated aniline salt (2 g) was separated and recrystallized from alcohol: the fine needles with m.p. 182–185° (with decomp.) were the aniline salt of chloromethylphosphinic acid. A mixed melting point of this substance and an authentic sample of the salt named was not depressed.

Found %: C 37.07, 37.13; H 5.53, 5.45; Cl 15.05, 15.33; N 7.48. $ClCH_2PO(OH)_2 \cdot C_6H_5NH_2$. Calculated %: C 37.60; H 4.03; Cl 15.90; N 6.26.

7. Action of phosphorus pentachloride on tri-(chloromethyl)-phosphorus oxide; preparation of tri-(trichloromethyl)-phosphorus hydroxychloride. 1 g of tri-(chloromethyl)-phosphorus oxide was mixed with 3 ml of phosphorus trichloride and 12 g of phosphorus pentachloride. The mixture was boiled gently for 30 minutes under reflux. Then the PCl_3 and $POCl_3$ were distilled off in vacuum, the residue treated with sulfur dioxide at room temperature and the filtrate sucked off. After treating the precipitate with hot water, we obtained 0.8 g of fine crystals, which separated as colorless needles with m.p. 200–202° (with decomp.) after two recrystallizations from benzine. The product did not contain chlorine, which was hydrolyzable under normal conditions. A mixed melting point with tri-(chloromethyl)-phosphorus hydroxychloride, obtained as described above, was not depressed.

Found %: Cl 81.16; P 7.78, 7.68. $(CCl_3)_3P(OH)Cl$. Calculated %: Cl 80.87; P 7.05.

8. Reaction of the diethyl ester of chloromethylphosphinic acid with triethyl phosphite. A mixture of 26.2 g of triethyl phosphite and 29.2 g of the diethyl ester of chloromethylphosphinic acid was heated for 8 hours at 185–190° in 3 ampules. Several distillations yielded the fractions: 1st b.p. 11.5–12.5°, 6.4 g; 2nd b.p. 70–

−90° (20 mm), 6.5 g; 3rd b.p. 90−95° (20 mm), 9.2 g; 4th b.p. 80−90° (4 mm), 4.1 g; 5th b.p. 90−95° (4 mm), 16.3 g; 6th b.p. 153−154° (3 mm), 12.1 g; total 54.6 g.

The boiling point and the molecular weight of 63.5 of the 1st fraction identified it as ethyl chloride. The 3rd fraction did not contain chlorine, had d^{20}_{20} 1.031, $n^{20}D$ 1.4155, and was the diethyl ester of ethylphosphinic acid.

Found %: C 43.60; H 9.27; OC_2H_5 53.75. M 159 (in benzene). $C_2H_5PO(OC_2H_5)_2$. Calculated %: C 43.40; H 9.05; OC_2H_5 54.2. M 166.

The 5th fraction was the starting diethyl ester of chloromethylphosphinic acid.

Found %: OC_2H_5 47.54. M 182 (in benzene). $ClCH_2PO(OC_2H_5)_2$. Calculated %: OC_2H_5 48.3. M 186.5.

The 6th fraction was a thick liquid, which did not contain chlorine, had d^{20}_{20} 1.167, $n^{20}D$ 1.4415 and was the tetraethyl ester of methylenediphosphinic acid.

Found %: 37.25, 37.34; H 6.75, 6.51; OC_2H_5 61.87, 61.99. M 292 (in benzene). $(C_2H_5O)_2P(O)CH_2PO(OC_2H_5)_2$. Calculated %: C 37.5; H 7.65; OC_2H_5 62.5. M 288.

Fractions 2 and 4 were intermediate.

Hydrolysis of tetraethyl ester of methylenediphosphinic acid. 1 g of material from the 6th fraction was boiled for 2 hours with 10 ml of 15% hydrochloric acid. Evaporation in vacuum and recrystallization from acetic acid yielded 0.2 g of methylenediphosphinic acid crystals with m.p. 199−200° [6].

9. Reaction of diethyl ester of β-chloroethylphosphinic acid with triethyl phosphite. A mixture of 12 g of the diethyl ester of β-chloroethylphosphinic acid and 28 g of triethyl phosphite was heated at 185−190° for 8 hours in sealed tubes. The reaction products, which contained ethyl chloride and the diethyl ester of ethylphosphinic acid, yielded a fraction with b.p. 170−175° (3 mm), 5.5 g, d^{20}_{20} 1.080, $n^{20}D$ 1.4425, which was the tetraethyl ester of ethylenediphosphinic acid.

Found %: OC_2H_5 58.75. M 308 (in benzene). $(C_2H_5O)_2P(O)CH_2CH_2PO(OC_2H_5)_2$. Calculated %: OC_2H_5 59.5. M 302.

10. Reaction of chloromethyltrimethylsilane with triethyl phosphite. A mixture of 12.3 g of triethyl phosphite and 10 g of chloromethyltrimethylsilane was heated at 170° for six hours in two ampules. We isolated 5.9 g of the diethyl ester of trimethylsilylmethylphosphinic acid with b.p. 79−80° (3 mm), d^{20}_{20} 0.9878, $n^{20}D$ 1.4280.

Found %: OC_2H_5 39.66, 39.46; P 13.11, 13.51; Si 12.37, 12.21. M 212.5 (in benzene). $(CH_3)_3SiCH_2PO(OC_2H_5)_2$. Calculated %: OC_2H_5 40.2; P 13.85; Si 12.5. M 224.

11. Reaction of triethyl phosphite with chloromethyltriethoxysilane. 10.25 g of chloromethyltriethoxysilane with b.p. 72−74° (12 mm) (prepared from chloromethyltrichlorosilane and alcohol in the presence of diethylaniline) and 8.0 g of triethyl phosphite were heated in an ampule as described in experiment 10. We isolated 15.5 g of the diethyl ester of triethoxysilylmethylphosphinic acid with b.p. 133−135° (3 mm), d^{20}_{20} 0.995.

Found %: OC_2H_5 69.97, 70.40; P 10.25, 9.85; Si 8.11, 7.95. M 299 (in benzene). $(C_2H_5O)_3SiCH_2PO(OC_2H_5)_2$. Calculated %: OC_2H_5 71.5; P 9.9; Si 8.9. M 314.

12. Reduction of trichloromethylphosphorus tetrachloride to trichloromethyldichlorophosphine. To a suspension of 12 g of trichloromethylphosphorus tetrachloride in 40 ml of dry carbon tetrachloride was added 0.5 g of phosphorus triiodide and with vigorous mixing in an atmosphere of nitrogen, a solution of 1.1 g of yellow phosphorus in 10 ml of carbon disulfide was added. A homogeneous liquid was quickly formed and the solvent was removed from this in vacuum; the residue was distilled. A second distillation yielded 5.5 g of colorless, hygroscopic crystals, which were readily oxidized in air and had b.p. 82−83° (7 mm) (with decomp.) and m.p. about 50−52°.

Found %: P 11.73, 11.27; Cl 81.85, 82.13 (combustion). M 238 (in benzene). CCl_3PCl_2. Calculated %: P 12.1; Cl 83.5. M 256.

0.5 g of the substance was left for 1 hour on a watch glass in a desiccator containing dry air. The crystals formed were treated with hot water. Removal of the water in vacuum gave 0.3 g of crystals with m.p. 77–79° (from CCl_4). A mixed melting point with authentic trichloromethylchlorophosphinic acid was not depressed.

1 g of the substance in 3 ml of dry ether was added dropwise (in nitrogen) to 10 ml of water, from which the oxygen had first been expelled by boiling in an atmosphere of nitrogen. After removing the solvent in vacuum, we obtained 0.3 g of a sirupy liquid. The substance gave calomel when heated with a solution of mercuric chloride. After boiling with nitric acid, the substance gave a positive molybdate test for phosphoric acid. Chloroform (isonitrile reaction with aniline) was present in the aqueous ether distillate.

SUMMARY

1. Using the reaction of chloromethyldichlorophosphine with diazomethane as an example, it was shown that this reaction did not give di- and tri-(chloromethyl)-phosphines.

Chlorination of the product obtained from the above reaction gave tri-(trichloromethyl)-phosphorus dichloride and di-(chloromethyl)-phosphinic and phosphoric acids (in the form of aniline salts). The scheme for the formation, and the structures of these compounds are discussed.

2. It was shown that the esters of chloromethyl- and β-chloroethylphosphinic acids undergo an Arbuzov reaction at high temperatures and form esters of methylene- and ethylenediphosphinic acids, respectively, with triethyl phosphite.

3. Chlorination of tri-(chloromethyl)-phosphorus oxide with phosphorus pentachloride gave tri-(trichloromethyl)-phosphorus dichloride which was hydrolyzed to tri-(trichloromethyl)-phosphorus hydroxychloride. This substance was stable to hydrolysis; when treated with aniline it was converted to tri-(trichloromethyl)-phosphorus oxide.

4. Trichloromethylphosphorus tetrachloride was reduced with yellow phosphorus to give trichloromethyldichlorophosphine, which split out chloroform when treated with water.

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IODO DERIVATIVES OF METHYLPHOSPHINE

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Iodides of organic acids of phosphorus have hitherto been represented only by phenylphosphine diiodide, obtained in the form of the hydroiodide by Michaelis [1] and Lecoq [2] by reaction of phenylphosphine dichloride with gaseous hydrogen iodide. It was found that alkylphosphine iodides can be prepared by reaction of acid chlorides of alkylphosphonic and alkylphosphonous acids with hydrogen iodide. This is illustrated in the present work by the preparation of iodo derivatives of methylphosphine. Treatment of methylphosphonic dichloride (in chloroform) with gaseous hydrogen iodide at room temperature gives dark-red crystals of an iodo derivative with m.p. 156°, whose composition corresponds to the formula CH_3PI_4. The compound is easily soluble in water with copious release of iodine and formation of methylphosphonic acid.

Phosphorus pentaiodide is known to be extremely unstable and cannot be isolated. Moreover, according to Fursman and Lipkin [3], some compounds of trivalent phosphorus, notably triphenyl phosphite, form a series of iodo derivatives with covalently bound iodine, including $(C_6H_5O)_3PI_4$ and $(C_6H_5O)_3PI_2$. We treated our prepared methylphosphorus tetraiodide with excess of dry sodium ethoxide with the aim of confirming its structure as a true compound of pentavalent phosphorus. Under conditions excluding oxidation this gave the diethyl ester of methylphosphonic acid. To a certain extent, this result rules out the possibility that this substance is the complex $CH_3PI_2 \cdot I_2$.

Apart from methylphosphorus tetraiodide, the reaction mixture gave (after distillation of the solvent) a resinous mass which evidently consisted of products of partial hydrolysis of acid chlorides present in the reaction medium. Treatment with water converts this mass into methylphosphonic acid. In a general way the process can be represented by the equation

$$3CH_3POCl_2 + 8HI \longrightarrow 2CH_3PI_4 + CH_3PO(OH)_2 + 6HCl$$

Reaction of hydrogen iodide with methyldichlorophosphine under similar conditions gives a crystalline product with m.p. 85–87°, outwardly resembling iodine and quite different in properties from the iodide described above. Its composition corresponds to the hydroiodide of methylphosphorus diiodide. Hardly any iodine is released when the compound dissolves in water, and the characteristic odor of phosphine is detected. It is evident that in reaction with hydrogen iodide aliphatic phosphonic dichlorides behave like aromatic compounds [1,2]:

$$CH_3PCl_2 \xrightarrow{3HI} CH_3PI_2 \cdot HI + 2HCl$$

Experiments on the reduction of methylphosphorus tetraiodide were undertaken with the objective of preparing free methylphosphine diiodide. The reduction was found to proceed with facility under the action of yellow phosphorus in a medium of carbon disulfide. Methylphosphine diiodide forms low-melting, cherry-red crystals; b.p. 68–70° (2 mm). It is hygroscopic; on treatment with aqueous alkali it releases methylphosphine. Fractional crystallization of the reaction mass gave in addition diphosphorus tetraiodide, possibly according to the equation:

$$2CH_3PI_4 + 2P \longrightarrow 2CH_3PI_2 + P_2I_4$$

Reaction of the resulting methylphosphorus diiodide with hydrogen iodide gave the hydroiodide with m.p. 85–86°, identical with the product of reaction of methylphosphorus dichloride with hydrogen iodide.

All of the investigated transformations in the series of methylphosphine iodides are represented by the scheme

$$CH_3POCl_2 \xrightarrow{HI} \underset{\text{m.p. 156°}}{CH_3PI_4} \xrightarrow{P} \underset{\text{b.p. 68–70°/ (2 mm)}}{CH_3PI_2} \xrightarrow{HI} CH_3PI_3 \cdot HI \longleftarrow CH_3PCl_2 + HI$$
$$\text{m.p. 87°}$$

During the course of this investigation papers were published by Walsh and co-workers that described the reduction of higher alkylphosphorus tetrachlorides to alkylphosphorus dichlorides under the action of yellow phosphorus [4,5]. These authors refer to the catalytic role of iodine in this reduction (in its absence the reaction reportedly does not take place). We found that iodides of phosphorus are readily reduced by yellow phosphorus in the absence of any catalyst. It was shown in particular that under the action of yellow phosphorus, phosphorus triiodide is quantitatively transformed into diphosphine tetraiodide. It is not excluded that the iodine is involved in an exchange reaction leading to intermediate formation of alkylphosphine iodides which easily react with yellow phosphorus.

EXPERIMENTAL

1. Interaction of methylphosphonic acid dichloride with hydrogen iodide. Preparation of methylphosphorus tetraiodide. Hydrogen iodide (dried over P_2O_5) was slowly bubbled into a solution of 20 g of methylphosphonic acid dichloride in 50 ml of dry chloroform at room temperature. The temperature in the reaction mixture rose to 45–50°, the solution acquired a red color, and cherry-red crystals were deposited. A total of 68 g of hydrogen iodide was passed through, of which 37 g combined. After 12 hours, the crystals were collected by decantation of the solvent, washed with dry chloroform and dried in vacuo. Yield 38.7 g with m.p. 156°.

Found %: P 6.00, 6.10; I 91.69, 91.94. M 545 ($POCl_3$). CH_3PI_4. Calculated %: P 5.6; I 91.64. M 554.

The yield of methylphosphorus tetraiodide was 97% (on the hydrogen iodide reacted). Further passage of hydrogen iodide led to resinification which complicated the purification of the substance. Removal of the chloroform from the solution left 13 g of viscous, resinous mass which after boiling with water was converted into methylphosphonic acid (9 g).

Hydrolysis of methylphosphorus tetraiodide. 5 g of CH_3PI_4 with m.p. 156° was dissolved in 200 ml of water. The solution was evaporated to dryness on a water bath and dried in a vacuum-desiccator over P_2O_5 to give 0.7 g of hygroscopic crystals with m.p. 99–100°, in agreement with the m.p. of methylphosphonic acid. 0.5 ml of aniline was run into 0.5 g of the acid and 5 ml of alcohol. The precipitated needles of the anilide were recrystallized from alcohol. M.p. 148–150°.

Found %: N 8.11, 8.15. $CH_3PO(OH)_2 \cdot C_6H_5NH_2$. Calculated %: N 7.41.

Reaction of methylphosphorus tetraiodide with dry sodium ethoxide. To a suspension of 10 g of dry, powdered sodium ethoxide in 50 ml of benzene was added 20 g of methylphosphorus tetraiodide with vigorous stirring. The temperature in the reaction mixture rose to +70° and the iodide lost its color. After 30 minutes the solution was filtered from the solid in a nitrogen atmosphere and fractionally distilled to give 1.75 g (35%) of the diethyl ester of methylphosphonic acid with b.p. 90–92° (10 mm), M 148 (in benzene), $d^{20}D$ 1.058, $n^{20}D$ 1.4138.

2. Reaction of methylphosphine dichloride with hydrogen iodide. Preparation of methylphosphine diiodide hydroiodide. Dry hydrogen iodide was bubbled at room temperature into a solution of 11.5 g of methylphosphine dichloride in 40 ml of dry chloroform. A little heat was generated during the reaction and crystals with the appearance of iodine came down. A total of 41.5 g of hydrogen iodide was passed through and 33.5 g reacted. The crystals were filtered off, washed with dry chloroform and dried in a current of carbon dioxide. Yield 28.2 g of substance with m.p. 85–87°. The yield was equivalent to 75% when calculated on the hydrogen iodide.

Found %: P 7.41, 7.31; I 88.50, 88.80. M 405 ($POCl_3$). $CH_3PI_2 \cdot HI$. Calculated %: P 7.25; I 89.0. M 428.

3. Reduction of methylphosphorus tetraiodide with yellow phosphorus. Preparation of methylphosphorus diiodide. 10.7 g of methylphosphorus tetraiodide (m.p. 156°) was added at room temperature to a solution of 0.6 g of yellow phosphorus in 15 ml of dry carbon disulfide. The iodide dissolved on shaking, and crystals of diphosphorus tetraiodide later came down. These were separated at room temperature and a further batch was obtained on freezing the filtrate in carbon dioxide. A total of 8.0 g of P_2I_4 was collected; m.p. 115–122°. After recrystallization from chloroform the m.p. was 123–124°.

3.5 g of a viscous, cherry-red liquid was obtained from the filtrate after evaporation in vacuo. After two distillations, 2.5 g of low-melting crystals with b.p. 68–70° (2 mm) was obtained.

Found %: P 9.60, 9.80; I 84.89, 85.11. M 295 (in benzene). CH_3PI_2. Calculated %: P 10.3; I 85.0. M 300.

Preparation of methylphosphine diiodide hydroiodide. A stream of dry hydrogen iodide was bubbled into a solution of 0.85 g of methylphosphine diiodide in 3 ml of dry chloroform until crystals ceased to come down. The crystals were separated, washed with dry chloroform and dried in vacuo. Yield 0.8 g of the hydroiodide with m.p. 85–86°. A mixture with a specimen prepared from methylphosphine dichloride did not give a depression of melting point.

4. Reduction of phosphorus triiodide with yellow phosphorus to diphosphorustetraiodide. To a solution of 0.3 g of yellow phosphorus in 10 ml of dry carbon disulfide was added 8 g of phosphorus triiodide (m.p. 61°). Orange crystals of P_2I_4 came down from the solution after 30 minutes; m.p. 124°; yield quantitative.

SUMMARY

1. Reaction of hydrogen iodide with chlorides of methylphosphonic and methylphosphonous acids gave the iodides CH_3PI_4 and $CH_3PI_2 \cdot HI$ which had not previously been described.

2. Reduction of methylphosphorus tetraiodide with yellow phosphorus gave methylphosphine diiodide. Under the same conditions phosphorus triiodide is quantitatively converted into diphosphorus tetraiodide.

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REACTIONS OF MAGNESYLAMINES

IV. ARYLAMIDATION OF AROMATIC ALDEHYDES WITH THE HELP OF ARYLAMINE-N,N-DIMAGNESIUM HALIDES

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In continuation of our work [1] on arylamidation of benzaldehyde with the help of arylamine-N,N-dimagnesium halides• we carried out the present investigation with the objective of extending the reaction to other aromatic aldehydes. In this connection it was necessary to establish the conditions that would considerably increase the yield of reaction products, since in the earlier work the yields of arylamides in the majority of cases did not exceed 15–18%.

Using aniline-N,N-dimagnesium bromide and p-toluidine-N,N-dimagnesium bromide as the amine component and benzaldehyde as the aldehydic component, it was shown that the solvent has an important influence on the yield of arylamides (Table 1). The table indicates that the yield of arylamides increases with the boiling point of the solvent (Experiments 1 to 4). The highest yields were obtained, however, by operating in pyridine and dioxan (Experiments 5 and 6). In the latter case the basic properties of the solvents may have favorably influenced the yield of benzarylamides.

TABLE 1

Preparation No.	Solvent	Yield (in %)	
		$C_6H_5CONHC_6H_5$	$C_6H_5CONHC_6H_4CH_3$-p
1	Ether	17.3	17.1
2	Benzene	19.8	18.8
3	Toluene	25.9	19.9
4	Xylene	40.6	33.6
5	Pyridine	51	48.5
6	Dioxan.	51.5	–

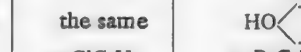
The duration of heating of the reaction mass also influences the yield of arylamides: the best results are obtained by 15-minutes' heating; longer heating leads to resinification.

Later experiments showed that the reaction that we had discovered for arylamidation of aldehydes with the help of dimagnesylamines can be successfully extended to various aromatic aldehydes (Table 2). We see from the data in this table that in the majority of cases arylamides are obtained in 50–90% yields and higher, so that our reaction can be said to stand comparison with the usual methods of preparative chemistry.

Arylamides (I-IX) have not been described in the literature; they are crystalline substances, sparingly soluble in ether, gasoline and chloroform, readily soluble in other organic solvents. The literature [4] reports m.p. 73° for the p-toluidide of p-chlorobenzoic acid (VIII) which is incorrect.

• Arylamine-N,N-dimagnesium halides will be called dimagnesylamines in the further course of this paper.

TABLE 2

Prep. no.	Aldehyde	Ar in ArN $(MgBr)_2$	Reaction product	Yield (%)	Type of crystals	Melting point [2]	Analysis for nitrogen (%) found	Analysis for nitrogen (%) calculated
1	p-$CH_3C_6H_4CHO$	C_6H_5	p-$CH_3C_6H_4CONHC_6H_5$	33.5	—	146°	—	—
2	p-BrC_6H_4CHO	the same	p-$BrC_6H_4CONHC_6H_5$	98.55	—	200—201	—	—
3	p-ClC_6H_4CHO	the same	p-$ClC_6H_4CONHC_6H_5$	83.8	—	194—195	—	—
4	p-$(CH_3)_2NC_6H_4CHO$	the same	p-$(CH_3)_2NC_6H_4CONHC_6H_5$	95.0	—	180—182	—	—
5	m-ClC_6H_4CHO	the same	m-$ClC_6H_4CONHC_6H_5$	91.1	—	136—137	—	—
6	p-$CH_3OC_6H_4CHO$	the same	p-$CH_3OC_6H_4CONHC_6H_5$	70.4	—	168—169	—	—
7	m-$CH_3C_6H_4CHO$	the same	m-$CH_3C_6H_4CONHC_6H_5$ (I)	53.3	Plates *	129—130	6.84, 6.73	6.63
8	m-BrC_6H_4CHO	the same	m-$BrC_6H_4CONHC_6H_5$	70	—	146—147.5	—	—
9	p-OH-(m-OCH_3)-C_6H_3CHO	the same	 (II)	53.5	Prisms**	129—131	5.52, 5.68	5.76
10	p-BrC_6H_4CHO	p-ClC_6H_4	p-$BrC_6H_4CONHC_6H_4Cl$-p (III)	69.7	Plates**	217—217.5	4.58, 4.47	4.51
11	the same	p-$CH_3C_6H_4$	p-$BrC_6H_4CONHC_6H_4CH_3$-p	64.4	—	232—233[3]	—	—
12	the same	p-BrC_6H_4	p-$BrC_6H_4CONHC_6H_4Br$-p	67.6	—	222	—	—
13	the same	p-$CH_3OC_6H_4$	p-$BrC_6H_4CONHC_6H_4OCH_3$-p (IV)	52.4	Plates**	222—223	4.50, 4.59	4.57
14	the same	α-$C_{10}H_7$	p-$BrC_6H_4CONHC_{10}H_7$-α (V)	51.5	Plates**	211—212	4.56	4.29
15	the same	β-$C_{10}H_7$	p-$BrC_6H_4CONHC_{10}H_7$-β (VI)	78.5	Needles	218—218.5	4.21, 4.26	4.29
16	p-ClC_6H_4CHO	β-$C_{10}H_7$	p-$ClC_6H_4CONHC_{10}H_7$-β (VII)	92.3	Plates**	206—207	5.06, 5.12	4.97
17	the same	p-$CH_3C_6H_4$	p-$ClC_6H_4CONHC_6H_4CH_3$-p (VIII)	50.5	Plates**	212—213	5.65, 5.54	5.70
18	the same	p-$CH_3OC_6H_4$	p-$ClC_6H_4CONHC_6H_4OCH_3$-p (IX)	53.5	Plates**	208—209	5.37, 5.24	5.35
19	the same	p-ClC_6H_4	p-$ClC_6H_4CONHC_6H_4Cl$-p	75.3	—	207—208	—	—

*Alcohol used as crystallization solvent.

**Acetic acid used for crystallization.

EXPERIMENTAL

Experimental procedure. Ethylmagnesium bromide was prepared from 0.025 mole of ethyl bromide and 0.025 mole of magnesium in 20 ml of ether. Addition was made to it of 0.0125 mole of aromatic amine in 15 ml of ether and the mixture was heated for 10–15 minutes on a water bath. The ether was driven off on a boiling water bath and a solution of 0.025 mole of aldehyde in 20 ml of dry pyridine was added to the residue; the mixture was then boiled for 5 minutes on a sand bath. The organomagnesium complex was decomposed with dilute hydrochloric acid and the reaction mass was twice treated with ether. The ether and the volatile products of reaction were distilled off with steam. The residue in the distillation flask was filtered, dried in the air and recrystallized from a suitable solvent. If a precipitate came down on decomposition of the organomagnesium complex, the precipitate was filtered, treated with steam and worked up as described above. In Experiment 9 (Table 2) the dimagnesylamine was taken in 1 : 1 ratio to the vanillin. The yield of arylamides was calculated on the aromatic amine taken into reaction.

A slightly modified procedure was employed for Experiments 1 to 4, 10 and 11 (Table 2). The ether was driven off from the ethylmagnesium bromide and a solution of the aromatic aldehyde in dry pyridine was added. To the resulting dimagnesylamine was added a pyridine solution of the aldehyde, the reaction mass was heated for 1 hour on the sand bath and decomposed with hydrochloric acid. The product was worked up as in the previous experiments.

The first procedure was found more convenient since less time was consumed both on the performance of the reaction itself and on the isolation of the reaction products. In addition the latter are obtained with higher purity and in satisfactory yields.

Beech's synthesis [5] of aromatic aldehydes. The aromatic aldehydes used in this work were prepared by Beech's method [5] with exception of p-dimethylaminobenzaldehyde and vanillin. His method was slightly modified. First, sodium acetate was not added to the solution of diazo compound, but the calculated quantity of the former was added to the solution of formaldehyde oxime. Secondly, hydrolysis of the oxime of the aldehyde was not performed directly in the reaction medium (as in Beech's procedure) but after its isolation. This leads to a considerable drop in the volume of the reaction mass and to shortening of the time needed for carrying out the experiment. Thirdly, prior to decomposition of the bisulfite compound the reaction mass was heated on a water bath until the dissolved ether had been completely removed. If the ether was not entirely removed, it was difficult to completely decompose the bisulfite compound and the yield of aldehyde was much lower.

SUMMARY

1. The effect of the nature of the solvent on the yield on arylamides of carboxylic acids was studied; it was found that the highest yields of arylamides are obtained when the experiments are performed in pyridine and dioxan.

2. The reaction of arylamidation of aldehydes with the help of dimagnesylamines was successfully extended to various aromatic aldehydes, and the optimum conditions for preparative employment of the reaction were established.

3. A number of previously undescribed arylamides of aromatic acids were prepared and their properties studied.

4. Beech's method of preparation of aromatic aldehydes was improved.

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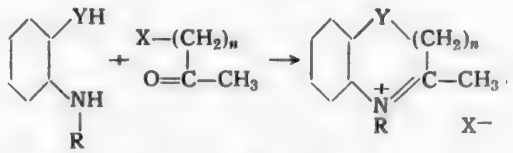
CONDENSATION OF o-AMINOTHIOPHENOLS WITH β-HALOKETONES

SYNTHESIS OF QUATERNARY SALTS IN THE DIHYDROBENZOHEPTA-1,5--THIAZINE SERIES. III

L. K. Mushkalo

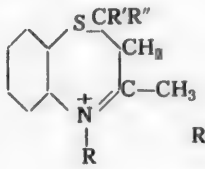
Quaternary salts of the dihydrobenzohepta-1,5-thiazine series are obtained by the usual method of alkylation of the corresponding bases, as well as by the action of mineral acids on derivatives of 5-alkyl- and 5-phenyldihydrobenzohepta-1,5-thiazines [1]. The yield of quaternary salts by this route does not exceed 50% reckoned on the original aminothiols. In the present communication we describe a new method of preparation of quaternary salts of seven-membered heterocycles by condensation of N-alkyl- and N-phenyl-o-aminothiophenols with β-haloketones.

This method is one case of a general method of preparation of quaternary salts of heterocyclic bases. As previously shown [2], condensation of N-alkyl- and N-phenyl-o-aminothiophenols and of N-substituted o-aminophenols with carboxylic acid chlorides gives quaternary salts of benzothiazole (or benzoxazole). If, however, the halogen is subsequently transferred from the carbonyl group to the halocarbonyl component, quaternary salts of six- and seven-membered heterocycles are obtained.



Y = S, O; X = halogen; R = alkyl, aryl; n = 0, 1, 2.

For example, condensation of N-alkyl- and N-aryl-o-aminothiophenols with α-haloketones (n = 1) gives quaternary salts of benzo-1,4-thiazine [2]; with β-haloketones, as we showed, quaternary salts of seven-membered heterocycles are formed.

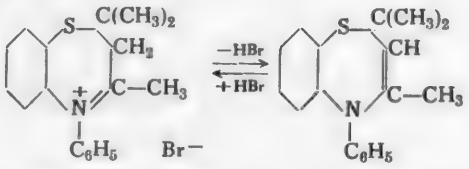


R=CH_3, C_2H_5, C_6H_5; R'and R"=H, CH_3.

This method gives good yields of quaternary salts, and it can be recommended for preparations of quaternary salts of the dihydrobenzohepta-1,5-thiazine series. Condensation of N-alkyl- and N-phenyl-o-aminothiophenols with methyl-β-bromoethyl ketone and its closest homologs proceeds with facility and with considerable evolution of heat. This reaction goes best of all in benzene solution.

Conversion of the quaternary salts to the perchlorates is recommended for their isolation and purification. The perchlorates crystallize easily. The yield of quaternary salts by this method reaches 70–90%.

The free bases can be isolated by treatment of quaternary salts of the dihydrobenzohepta-1,5-thiazine series with an aqueous solution of caustic alkali. Alkali treatment, for example, of an aqueous solution of the phenobromide of 2,2,4-trimethyldihydrobenzohepta-1,5-thiazine gives the crystalline base, which with mineral acids again gives the original quaternary salt.



The methyl group in the 4-position of these salts possesses active hydrogen atoms. Our synthesized quaternary salts can accordingly be employed for the synthesis of cyanine dyes [3].

EXPERIMENTAL

Phenobromide of 2,2,4-trimethyldihydrobenzohepta-1,5-thiazine. A mixture of 2.1 g of N-phenyl-o-aminothiophenol, 1.8 g of freshly distilled methyl β-bromoisobutyl ketone and 3 ml of benzene was heated on a water bath. The resulting exothermic reaction was completed in a few seconds. The bottom layer, containing the quaternary salt, was separated and a few milliliters of acetone was added. Rubbing with a glass rod caused the quaternary salt to crystallize. The crystals were filtered and washed successively with acetone and alcohol. Yield of phenobromide of 2,2,4-trimethyldihydrobenzohepta-1,5-thiazine 3.6 g (70%), m.p. 147°.

Found %: Br 22.10, 22.37. $C_{18}H_{20}SNBr$. Calculated %: Br 22.09.

2,2,4-Trimethyl-5-phenyldihydrobenzohepta-1,5-thiazine. An aqueous solution of 0.6 g of the phenobromide of 2,2,4-trimethyldihydrobenzohepta-1,5-thiazine was shaken with aqueous caustic alkali. The liberated base was extracted with ether and dried with solid potassium hydroxide. The base crystallized after the ether had evaporated. Yield 0.2 g of 2,2,4-trimethyl-5-phenyldihydrobenzohepta-1,5-thiazine with m.p. 97°.

Found %: N 4.96, 5.02. $C_{18}H_{19}NS$. Calculated %: N 4.95.

With perchloric acid the base forms a quaternary salt—the phenoperchlorate of 2,2,4-trimethyldihydrobenzohepta-1,5-thiazine with m.p. 190°.

Methoperchlorate of 2,4-dimethyldihydrobenzohepta-1,5-thiazine. A mixture of 5 g of N-methyl-o-aminothiophenol, 6.5 g of freshly distilled methyl β-bromopropyl ketone and 5 ml of benzene was heated on a water bath for 20 minutes. The lower layer of quaternary salt weighed 7.7 g (70%) and was a vitreous mass which did not crystallize. The perchlorate of the quaternary salt was prepared by treating an alcoholic solution of the methobromide of 2,4-dimethyldihydrobenzohepta-1,5-thiazine with perchloric acid. After recrystallization from alcohol, the crystals of methoperchlorate of 2,4-dimethyldihydrobenzohepta-1,5-thiazine had m.p. 111° and were identical with the methoperchlorate of 2,4-dimethyldihydrobenzohepta-1,5-thiazine prepared from 2,4,5-trimethyldihydrobenzohepta-1,5-thiazine and perchloric acid [1].

Phenoperchlorate of 2,4-dimethyldihydrobenzohepta-1,5-thiazine. 2.4 g of N-phenyl-o-aminothiophenol was mixed with 3 ml of benzene and 2 g of freshly distilled methyl β-bromopropyl ketone. An exothermic reaction commenced in a few minutes and the contents of the test tube formed two layers. The lower layer of quaternary salt was separated from the upper benzene layer and washed with benzene and ether. Yield of phenobromide of 2,4-dimethyldihydrobenzohepta-1,5-thiazine 4 g (95%). The quaternary salt is a vitreous mass. The perchlorate was obtained by the action of 30% perchloric acid on an alcoholic solution of the quaternary salt. After recrystallization from alcohol, the phenoperchlorate of 2,4-dimethyldihydrobenzohepta-1,5-thiazine had m.p. 198°.

Found %: Cl 9.82, 9.70. $C_{17}H_{18}O_4NSCl$. Calculated %: Cl 9.68.

Phenobromide of 4-methyldihydrobenzohepta-1,5-thiazine. To a solution of 2 g of N-phenyl-o-aminothiophenol in 2 ml of benzene was added 1.5 g of freshly distilled methyl β-bromoethyl ketone. Heat was liberated and the exothermic reaction quickly came to an end. After heating for 10 minutes on a water bath,

the lower layer of quaternary salt was separated from the upper benzene layer and washed with benzene and ether. After drying in an extractor over paraffin wax, the quaternary salt was a colorless, vitreous mass which was perfectly pure and suitable for the preparation of dyes. Yield of phenobromide of 4-methyldihydrobenzohepta-1,5-thiazine 3 g (87%).

Found %: Br 24.05. $C_{16}H_{16}NSBr$. Calculated %: Br 23.93.

The phenoperchlorate of 4-methyldihydrobenzohepta-1,5-thiazine, prepared in the usual manner from the phenobromide of 4-methyldihydrobenzohepta-1,5-thiazine and perchloric acid, was isolated in crystalline form. It has m.p. 163° and is identical with the phenoperchlorate of 4-methyldihydrobenzohepta-1,5-thiazine that we previously prepared [1] from 4-methyl-5-phenyldihydrobenzohepta-1,5-thiazine and perchloric acid.

SUMMARY

1. A new method is proposed for preparation of quaternary salts of seven-membered heterocyclic compounds which consists in condensation of N-alkyl- and N-phenyl-o-aminophenylmercaptans with β-haloketones. It can be recommended as a preparative method for quaternary salts of the dihydrobenzohepta-1,5-thiazine series.

2. The new method was employed for the preparation of 4 new quaternary salts in the dihydrobenzohepta-1,5-thiazine series which had not previously been described in the literature.

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REACTION OF DIAZO COMPOUNDS WITH SULFAMIC ACID AND ITS DERIVATIVES

VII. REACTION OF DIAZO COMPOUNDS WITH UNSUBSTITUTED SULFAMIC ACID

D.Z. Zavel'skii and L.A. Lishnevskaia

It was previously [1] shown that unsubstituted sulfamic acid reacts only with active diazo compounds, i.e. those containing electron-accepting groups (NO_2, Cl, etc.). This does not lead, however, to the expected aryltriazene-N-sulfonic acids but to the amine or symmetrical diaryltriazene corresponding to the diazo compound. We explained this reaction by a scheme whereby unstable aryltriazene-N-sulfonic acids are first formed and slowly break down to give nitrogen, sulfur trioxide and amine; if the amine is sufficiently active in the diazoamino condensation, it is capable of forming a symmetrical diaryltriazene with the diazo compound present.

$$ArN_2OH + NH_2SO_3Na \longrightarrow ArN{=}N{-}NHSO_3Na + H_2O \quad (1)$$

$$ArN{=}N{-}NHSO_3Na \xrightarrow{H_2O} ArN{=}N{-}NH_2 + HOSO_3Na \quad (2)$$

$$ArN{=}N{-}NH_2 \longrightarrow ArNH_2 + N_2 \quad (3)$$

$$ArNH_2 + ArN_2OH \longrightarrow ArNH{-}N{=}NAr + H_2O \quad (4)$$

The correctness of the above mechanism was confirmed by the fact that by reaction of diazo compounds with N-methylsulfamic acid we obtained [2] products of the diazoamino condensation—methylaryltriazene-N--sulfonates—which had adequate stability but were susceptible to breakdown in an acid medium in the following manner:

$$ArN{=}N{-}N\begin{matrix}CH_3\\SO_3Na\end{matrix} \xrightarrow{H_2O} \begin{matrix}ArN_2OH + HN\begin{matrix}CH_3\\SO_3Na\end{matrix}\\ArN{=}N{-}NHCH_3 + HOSO_3Na\end{matrix} \quad (5)$$

$$ArN{=}N{-}NHCH_3 \rightleftarrows ArNH{-}N{=}NCH_3 \xrightarrow[+H_2O]{} \begin{matrix}ArNHCH_3 + N_2\\ArNH_2 + N_2 + CH_3OH\end{matrix} \quad (6)$$

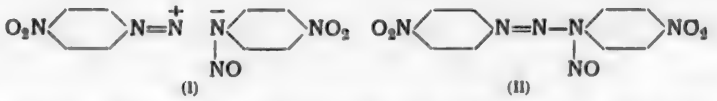
Further confirmation of the proposed mechanism of reaction of diazo compounds with unsubstituted sulfamic acid was afforded by our study [3] of the reaction of formation and breakdown of labile diaryltriazene-N-sulfonates with formation of unsymmetrical diaryltriazenes.

$$ArN_2OH + Ar'NHSO_3Na \longrightarrow ArN{=}N{-}N\begin{matrix}Ar'\\SO_3Na\end{matrix} + H_2O \quad (7)$$

$$ArN{=}N{-}N\begin{matrix}Ar'\\SO_3Na\end{matrix} + H_2O \longrightarrow ArN{=}N{-}NHAr' + HOSO_3Na \quad (8)$$

Grimmel and Morgan [4] used sulfamic acid as the agent for removal of excess of nitrous acid during diazotization of amines [5] and also observed that it reacts with very negatively substituted diazo compounds in an acid medium with formation of nitrogen, sulfuric acid and starting arylamine. The authors considered three variants of an explanation of the mechanism of the reaction and reached the conclusion that the most probable mechanism is that advanced above (Equations 1 to 3).

Other conclusions may be reached on the basis of the work of I. V. Grachev and B. A. Porai-Koshits [6]. These authors found that in a neutral medium diazo compounds release nitrous acid with formation of diaryltriazenes. On the basis of this observation and of the results of potentiometric titration, the authors concluded that in a neutral medium diazo compounds exist as salts [diazonitrosaminates (I)] or covalent compounds [diaryl-N-nitrosotriazenes (II)].

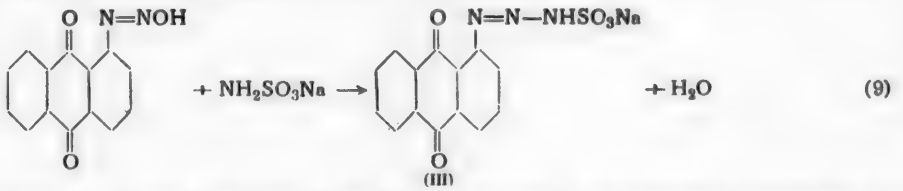


(I) (II)

In the authors' opinion, these compounds are capable of splitting off the nitroso group just as easily as diaryltriazene-N-sulfonates split off the sulfo group. In the light of the ideas of I. V. Grachev and B. A. Porai-Koshits, it is logical to assume that sulfamic acid differs from its monosubstituted derivatives in not entering into the diazoamino condensation with diazo compounds according to reaction (1) and that it is only an acceptor of nitrous acid which splits off from compounds of the type of (I) and (II).

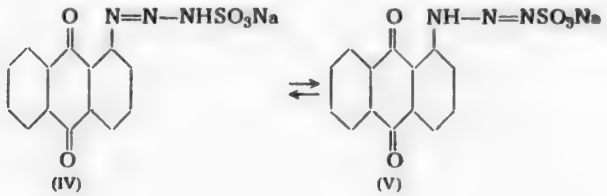
Wishing to obtain direct proof of the ability of unsubstituted sulfamic acid to undergo the diazoamino condensation and having obtained negative results with diazo compounds of the benzene series, we tried to bring it into reaction with 1-diazoanthraquinone. This attempt was prompted by the known fact that no diazo compound of the benzene series is capable of forming the corresponding stable triazenes with ammonia, hydroxylamine or hydrazine, whereas 1-diazoanthraquinone (as well as some derivatives) is capable of giving triazenes with these substances, as was shown by Wacker [7].

Experiment showed that at a pH of 6 to 8.5 it is possible to condense 1-diazoanthraquinone with sulfamic acid to give an 80–85% yield of 1-anthraquinonyltriazene-3-sulfonate (III).

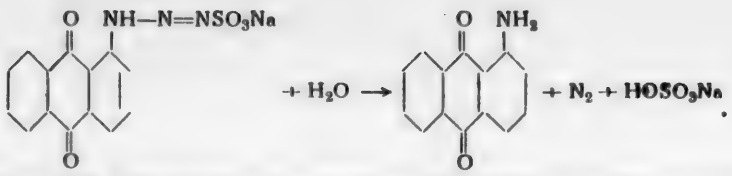


(III) (9)

After recrystallization from water the product is free of sodium acetate, but is unstable in storage and when heated in the dry form or in aqueous solution. On decomposition it forms 1-aminoanthraquinone, bisulfate and nitrogen. The same products result immediately on addition of mineral acid to the cold aqueous solution of the triazene; the same process occurs, but slowly, when acetic acid is added. The decomposition of 1-anthraquinonyltriazene-N-sulfonate is readily accounted for by the hypothesis that the triazene with the structure (IV) (as indicated by the synthesis) undergoes tautomeric rearrangement to form (V) which irreversibly breaks down according to equation (11), so that equilibrium (10) is shifted to the right.



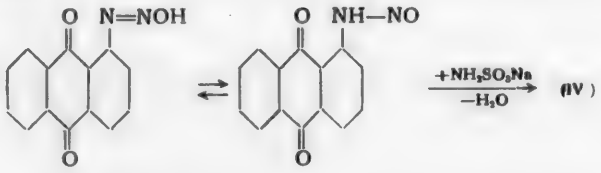
(IV) (V) (10)



(11)

The experiment with 1-diazoanthraquinone has thus afforded direct proof that unsubstituted sulfamic acid is capable of reacting with diazo compounds in the capacity of an amino component and not in the capacity of an acceptor of nitrous acid.

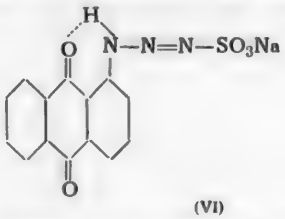
The hypothesis that 1-diazoanthraquinone reacts with sulfamic acid in the form of a nitrosamine with formation directly of the tautomer (IV)



(12)

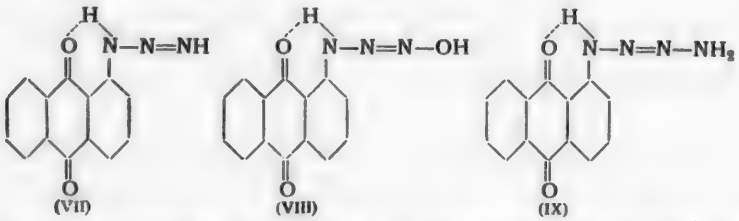
must be considered unproven since on prolonged stirring of specially synthesized ethylphenylnitrosaminate [8] and ethyl-(4-nitrophenyl)-nitrosaminate [9] in aqueous or aqueous alcoholic solution with sodium sulfamate we failed to observe any signs of the formation of a triazene.

It was found that 1-anthraquinonyltriazene-N-sulfonate is incapable of coupling with hydroxy- or aminoazo components in a medium of acetic acid or mineral acid in a similar manner to ordinary triazenes. On this basis we may suggest that the tautomer (IV), formed during synthesis, isomerizes to (V) in which the proximity of the anthraquinone carbonyl causes the compound to be stabilized in the form of (VI) with a hydrogen bond.



(VI)

This hypothesis may account for the incapability of existence, not discussed by Wacker [7], of products of the diazoamino condensation of diazo compounds of the benzene series with ammonia, hydroxylamine and hydrazine, whereas the corresponding derivatives of α-diazoanthraquinone are quite stable. In this case also we can suggest that these anthraquinonyltriazenes are stabilized by the formation of a hydrogen bond between the labile hydrogen of the triazene group and the carbonyl oxygen.



(VII) (VIII) (IX)

With the objective of obtaining further proof of the correctness of the hypothesis that 1-anthraquinonyltriazene-N-sulfonate exists in the form of tautomer (IV) or (V), we performed its methylation with dimethyl sulfate in an alkaline medium. 1-Diazoanthraquinone was not detected when the product of methylation was acidified. The reaction accordingly did not proceed according to the scheme:

$$AxN{=}N{-}NHSO_3Na + (CH_3)_2SO_4 \longrightarrow AxN{=}N{-}N\begin{matrix}CH_3\\SO_3Na\end{matrix}$$

$$AxN{=}N(HO)(H)N\begin{matrix}CH_3\\SO_3Na\end{matrix} \xrightarrow{HCl} AxN_2OH + NH\begin{matrix}CH_3\\SO_3Na\end{matrix}$$

The red product coming down on acidification was a mixture of 1-methylaminoanthraquinone and 1-aminoanthraquinone. Treatment of the mixture with nitrite in concentrated hydrochloric acid gave 1-diazoanthraquinone, which went into solution, and a nitroso derivative of 1-methylaminoanthraquinone which remained undissolved. The nitroso product gave a positive reaction in the Liebermann test. Hydrolysis of the nitroso product with concentrated hydrochloric acid at the boil gave 1-methylaminoanthraquinone whose melting point was the same as that of a mixture (165–167°) with an authentic specimen of 1-methylaminoanthraquinone synthesized by Lauer's method [10]. The reactions

$$AxNH{-}N{=}N{-}\underset{(V)}{SO_3Na} + (CH_3)_2SO_4 \longrightarrow AxN(CH_3){-}N{=}NSO_3Na + CH_3NaSO_4 \qquad (13)$$

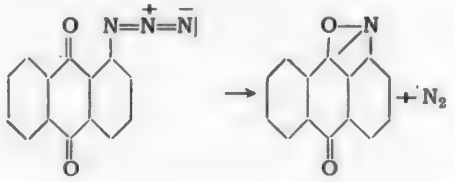
$$AxN(CH_3){-}N{=}NSO_3Na \xrightarrow{HOH} AxNHCH_3 + N_2 + NaHSO_4 \qquad (14)$$

$$AxNHCH_3 + HONO \longrightarrow AxN\begin{matrix}CH_3\\NO\end{matrix} + H_2O \xrightarrow{HCl} AxNH{-}CH_3 + HONO \qquad (15)$$

confirm that 1-anthraquinonyltriazene-N-sulfonate exists in the form of the tautomer (V) or (VI). During methylation of the triazene it was noted that it dissolves in dilute alkali with a dark-red color and after a short time it deposits a light-brown substance. It was established that even at room temperature alkali nearly quantitatively cleaves 1-anthraquinonyltriazene-N-sulfonate into anthraquinonyl azide and sulfurous acid:

$$AxNH{-}N{=}NSO_3Na \longrightarrow AxN_3 + HSO_3Na \qquad (16)$$

1-Anthraquinonyl azide was identified by its appearance (stout, brownish-yellow needles), elementary analysis, and reactions, the most characteristic of which is the transformation into anthranyl by a slight modification of the procedure of Gattermann and Ebert [11].

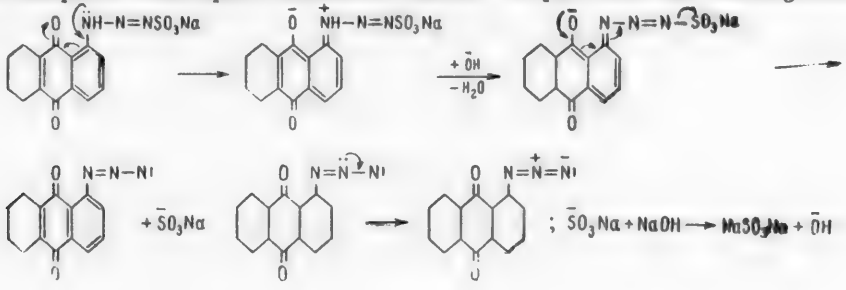


(17)

The smooth and facile hydrolysis of 1-anthraquinonyltriazene-N-sulfonate to 1-anthraquinonyl azide and sulfur dioxide is similar in character to the hydrolysis with alkali of the products of coupling of diazo compounds with aryl- or alkylsulfamides to form aryl azides and sulfinic acid. The latter reaction was studied by Dutt and co-workers [12].

$$ArN{=}N{-}NHSO_2R \xrightarrow{NaOH} ArN_3 + RSO_2H \qquad (18)$$

It is an example of a nucleophilic substitution reaction. We put forward the following reaction mechanism:



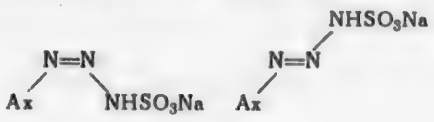
Due to the electrophilic character of the carbonyl group of anthraquinone, a positive charge is at first formed at the nitrogen. This causes the hydrogen at the nitrogen to be protonized and to react with hydroxyl to form water. The negative charge at the carbonyl is transmitted along the chain of conjugated bonds to the end nitrogen, resulting in cleavage of the anion of sulfurous acid. The anthraquinonyl residue with three conjugated nitrogens is stabilized in the form of 1-anthraquinonylazide.

Consequently, under the action of alkali anthraquinonyltriazene-N-sulfonate undergoes an intramolecular oxidation–reduction reaction, the sulfo group being reduced to sulfurous acid while the anthraquinonyltriazene residue is oxidized to anthraquinonyl azide.

The two forms of 1-anthraquinonyltriazene-N-sulfonate. It was recalled earlier that freshly recrystallized triazenesulfonate (yellow) fairly quickly turns red in storage. The red product is completely soluble in water, but both in the dry state and in solution it is very much less stable than the yellow form, and tends even without acidification to break down to 1-aminoanthraquinone, nitrogen and sulfur trioxide. The light-red form is more soluble than the yellow form in alcohol.

All attempts to throw light on the behavior of the yellow and red forms towards chemical reagents remained without result. It could only be established that the red form was less resistant to impact than the yellow; the former is decomposed by each impact by a weight of 10 kg from a height of 20 cm, while the second form is not.

Physicochemical methods, in particular optical methods of investigation are suggested for clarification of the difference in structures of the yellow and red forms. It may be suggested that the two forms of the triazenesulfonate are cis- and trans-isomers, in analogy with Gattermann's findings for azoanthraquinone [11].



EXPERIMENTAL

Diazotization of 1-aminoanthraquinone. Schaarschmidt's procedure [13] was used with slight modifications. 2.21 g of 1-aminoanthraquinone was triturated with 20 ml of concentrated hydrochloric acid. After 10-minutes' stirring, 2.2 ml of 5 N sodium nitrite solution was introduced under the surface of the liquid at room temperature. After red amine had ceased to separate on dilution of a drop of reaction solution with water, the reaction mass was cooled and the precipitated diazochloride was filtered off.

The diazochloride slurry was recrystallized from 15–20 times the volume of water at 60–70°. Large crystals of 1-anthraquinonyl diazonium chloride came down on cooling with ice. They were filtered, washed with cold alcohol and then with ether, and dried in a vacuum-desiccator over caustic alkali and paraffin wax. Yield of recrystallized diazonium compound 1.63 g.

Condensation of 1-diazoanthraquinone with sulfamic acid. 2.38 g of sodium sulfamate was dissolved in 10 ml of concentrated acetate buffer with a pH of 6; a solution of 2.7 g of 1-anthraquinonyl diazonium chloride saturated at room temperature was then added in one portion. The reaction mass gradually deposited a light-brown precipitate. The pH of the mixture was brought to 8.0–8.5 by addition of bicarbonate and subsequently kept at this level. The pH of the solution ceased to fall in 1–2 hours after the start of the experiment, and the compound ceased to give a reaction for an active diazo compound with H-acid, although the precipitate from the reaction mixture only ceased to give an active diazo reaction after stirring for 16–18 hours. A few grams of sodium acetate were then added to the reaction mixture to improve the salting-out; the product was cooled with ice, filtered, and dried in a desiccator or in the air at room temperature. Yield 3.5 g (purity 81.2%). The sodium salt of 1-anthraquinonyltriazene-3-sulfonic acid (containing acetate) can be kept unchanged for several days. It dissolves almost completely in water.

The salt was recrystallized from 20–25 times the quantity of water heated to 50–55°. The yellow, crystalline precipitate acquired a golden-orange tint during filtration. The product was washed with initially ice-cooled water, then with alcohol and ether, and thoroughly pressed before being dried in a thermostat at 40–50° for 10–15 minutes with continuous stirring. The product reddens and sometimes decomposes if dried slowly in a vacuum-desiccator over caustic alkali.

Properties of sodium 1-anthraquinonyltriazene-3-sulfonate. Lustrous, yellow or golden-orange crystals with the form of flat needles or elongated plates under the microscope. Readily soluble in water (the solution has a yellow color), less easily soluble in alcohol, and very sparingly soluble in ether.

In the pure form the sodium salt of the triazene-N-sulfonic acid is remarkably unstable. Preparations can with luck be kept in vacuo at room temperature for some hours without change. They often decompose, however, even during drying or a few minutes after drying. A sign of the start of breakdown is reddening, while the completion of decomposition is marked by conversion into a water-insoluble product. At the same time the compound gives off nitrogen, and the substance develops an acid reaction to Congo. An aqueous extract of the decomposed product gives an abundant precipitate of barium sulfate with barium chloride.

Heating of the dry preparation to 50–60° in an open test tube leads to instantaneous decomposition, and drops of water are deposited on the walls.

Heating of an aqueous solution of the triazene sulfonate to above 50° causes it to gradually turn bright-red, and a gel of fine precipitate is formed. Addition of sodium acetate to the aqueous solution raises the temperature of decomposition. A red precipitate comes down quickly when mineral acid is added to a cold solution of the triazene. The same decomposition occurs after several hours when acetic acid is added.

After one recrystallization, the red precipitate resulting from decomposition of the triazene sulfonate has m.p. 246°. It is very pure 1-aminoanthraquinone.

The triazene-N-sulfonate does not couple with azo components either in neutral, acetic acid or mineral acid media.

Analysis of sodium anthraquinonyltriazene-N-sulfonate. Water of crystallization. A weighed sample was put into a crucible with a lid and left to break down spontaneously. The crucible was then placed in a thermostat at 110° until the weight was constant.

The calculation was based on the equation of decomposition:

$$C_6H_4(CO)_2C_6H_3N_2{-}NHSO_3Na \cdot nH_2O = C_6H_4(CO)_2C_6H_3NH_2 + NaHSO_4 + N_2 + (n-1)H_2O.$$

Found %: loss of weight 15.06, 15.36. With n = 3, calculated %: loss of weight 15.72.

The compound therefore contains 3 molecules of water of crystallization.

Diazo nitrogen. A weighed sample of the substance was placed in the flask of an apparatus for determination of diazo nitrogen and several milliliters of concentrated sodium acetate solution were added. Air was flushed out of the apparatus with carbon dioxide, after which 50 ml of 50% sulfuric acid was poured into the flask. The solution quickly turned red and an upper layer of 1-aminoanthraquinone was formed. Nitrogen was driven off by boiling.

Found %: diazo nitrogen 6.88, 6.81. $C_{14}H_8O_5N_3SNa \cdot 3H_2O$. Calculated %: diazo nitrogen 6.88.

Sodium. The residue in the flask after determination of crystal water was moistened with sulfuric acid and ashed.

Found %: Na 5.62, 5.57. $C_{14}H_8O_5N_3SNa \cdot 3H_2O$. Calculated %: Na 5.65.

Sulfur (by Carius and Messinger methods).

Found %: S 8.05, 7.92. $C_{14}H_8O_5N_3SNa \cdot 3H_2O$. Calculated %: S 7.87.

Carbon and hydrogen. A tube was filled with fused lead chromate. A weighed sample of the compound was mixed with pulverized potassium dichromate and lead chromate (previously dried by heating to 700° in a nitrogen stream) and placed in a boat of oxidized copper 20 cm long. Small portions of this mixture were separated from one another by layers of lead chromate or copper oxide.

Found %: C 41.48, 41.43; H 3.27, 3.32. $C_{14}H_8O_5N_3SNa \cdot 3H_2O$. Calculated %: C 41.28; H 3.47.

Nitrogen (Dumas determination).

Found %: N 10.37, 10.21. $C_{14}H_8O_5N_3SNa \cdot 3H_2O$. Calculated %: N 10.32.

Methylation of sodium 1-anthraquinonyltriazene sulfonate. 4.07 g of the compound was suspended in 20 ml of water, and 6.3 g of dimethyl sulfate, previously treated with sodium carbonate until the acid reaction had disappeared, was run in. During the methylation an alkaline reaction was maintained by gradual addition of sodium hydroxide. After it had been stirred for 8 hours, the alkaline solution was left overnight. The resulting light-brown, viscous mass was acidified with hydrochloric acid while heating. The red precipitate was filtered off. The filtrate did not couple with azo components and did not take up nitrite; therefore it did not contain diazoanthraquinone and sulfamic (or methylsulfamic) acid. The red precipitate was washed, pressed, mixed with concentrated hydrochloric acid and treated with excess of 5 N nitrite. Part of the solid went into solution and part acquired a sandy color. The reaction mixture was filtered. 1-Diazoanthraquinone was detected in the filtrate (coupling with R-salt). The precipitate was washed with hydrochloric acid, then with water (until the reaction for nitric acid was absent) and dried. It then weighed 0.7 g. On fusion of a sample with phenol and sulfuric acid, the melt became intensely green; when the melt was poured into water the mixture turned red, while addition of alkali changed the color to blue. With diphenylamine in sulfuric acid a sample of the precipitate gave a deep-blue coloration. Both of the reactions identify the substance as a nitrosamine.

0.5 g of the nitrosamine was hydrolyzed by boiling with 5 ml of concentrated hydrochloric acid. The light-brown suspension darkened and went into solution with a brownish-red color. The small quantity of dark precipitate was filtered and 50 ml of water was added to the filtrate. A dark-red flocculent precipitate came down and the liquid became nearly colorless. The precipitate was filtered, washed with water and dried. After recrystallization from alcohol and then from benzine it had m.p. 165–167°. A mixture with authentic 1-methylaminoanthraquinone (m.p. 166°) melted at 165–167°. Consequently hydrolysis of the nitroso product had led to formation of methylaminoanthraquinone.

Reaction of sodium 1-anthraquinonyltriazene sulfonate with alkali. a) Preparation of 1-anthraquinonyl azide. To 4.07 g of the triazene sulfonate, mixed with 120 ml of water, was added 3-4 ml of 40% sodium hydroxide. The reaction mixture turned dark-red, and the solid went into solution after a few minutes. A dark substance started to come down quickly. In an hour after addition of the alkali, the solid was filtered off, washed with water and dried in the air. The light-brown product weighed 3.36 g. Careful recrystallization from hot methanol in presence of active carbon gave brownish-yellow needles (under the microscope the crystals had the form of stout needles and elongated prisms). For analytical purposes it was recrystallized again from methanol and dried in a vacuum-desiccator over potassium hydroxide.

Found %: N 16.62, 16.47. $C_{14}H_7O_2N_3$. Calculated %: N 16.86.

After a few days in the air or a desiccator, the lustrous crystals became dull and crumbly. Examination under the microscope revealed, apart from yellow needles and prisms of azide, fine crystals of indeterminate form and with a deeper reddish tone.

b) Determination of sulfur dioxide. A weighed sample of the triazene was stirred with 8 ml of water and 0.8 ml of 40% sodium hydroxide solution at 50–60° for 20 minutes. A precipitate came down on cooling and was filtered. The filtrate was acidified with sulfuric acid and the sulfur dioxide was driven off into alkali solution. The SO_2 content of the distillate was determined by iodometry.

Found %: SO_2 15.9. $C_{14}H_9O_5N_3SNa \cdot 3H_2O$. Calculated %: SO_2 15.7.

c) Conversion of 1-anthraquinonyl azide into anthranil (benzopseudoxazole). A weighed sample of anthraquinonyl azide was placed in a small flask connected to a nitrometer filled with potassium hydroxide solution. 50 ml of xylene was added, air was purged out of the system by a stream of CO_2, and the mixture was heated to the boil. Evolution of gas was complete after boiling for 5 minutes.

Found %: diazo nitrogen 10.5. $C_{14}H_7O_2N_3$. Calculated %: diazo nitrogen 11.24.

Crystals were deposited from the xylene solution remaining in the flask. They were filtered, washed and dried. Under the microscope they appeared as stout, orange prisms. They did not have a sharp melting point.

Found %: N 6.44. $C_{14}H_7O_2N$. Calculated %: N 6.33.

A specimen of the anthranil was heated with concentrated sulfuric acid and the solution was poured on to ice. The resulting dark-red precipitate was identified as 1-amino-4-hydroxyanthraquinone. This reaction is characteristic of anthranil [7, 11].

The two forms of sodium anthraquinonyltriazene-N-sulfonate. On recrystallization of the triazene from water at 55°, a yellow suspension was obtained which consists of yellow, elongated plates. During filtration the substance turned pink with a tinge of gold. The substance became a deeper red after pressing between sheets of filter paper and drying in a vacuum-desiccator over solid alkali. However, the form of the crystals and their ability to dissolve completely in water remained unchanged. If the light-red product was treated with alcohol before drying, the alcohol acquired an orange color and the solid again turned yellow. After filtration, washing with ether, and drying for 1.5 hours in a vacuum-desiccator, the egg-yellow product again turned red and approached the color of the basic product prior to treatment with alcohol. This reddened product was likewise completely soluble in water, but its aqueous solution was very unstable. After only a few minutes it started to give off nitrogen and deposited red 1-aminoanthraquinone. After the reddened product had been in a desiccator for several hours, and had then been treated with alcohol, intensive evolution of nitrogen commenced and aminoanthraquinone came down.

The light-red product was kept for 2.5 hours in the desiccator and then treated with alcohol. The resulting yellow product was filtered and recrystallized from water. During filtration, pressing and drying, the crystals again acquired a light-red color with a golden tinge. The operations of treatment with alcohol and recrystallization could be repeated many times to give, from the same substance, sometimes the egg-yellow and sometimes the light-red form of the triazene-N-sulfonate.

It was established that the yellow form is appreciably more stable in store than the red form. In some experiments the yellow form that had been kept in a vacuum-desiccator remained completely soluble in water for 24 hours although it turned slightly red. The red form of the triazene prepared from the identical starting substance decomposed under these conditions in the course of 2–3 hours.

It was observed that 1-anthraquinonyltriazene-N-sulfonate decomposes instantaneously under impact with formation of 1-anthraquinone which becomes enveloped in a red cloud due to the vigorous release of nitrogen. The yellow and red forms of the substance were tested for sensitivity to shock with the help of a drop hammer usually employed for testing of explosives. It was found that with a load of 10 kg and a height of fall of 20 cm the red substance is decomposed with formation of 1-aminoanthraquinone 25 times out of 25 tests. Under these conditions the yellow form began to decompose only after turning red in storage. Consequently the yellow form is more resistant than the red form to shock and to spontaneous decomposition.

SUMMARY

1. A mechanism of the reaction between diazo compounds and unsubstituted sulfamic acid is put forward and discussed. It postulates the initial formation of an aryltriazene-N-sulfonic acid which tautomerizes to a labile form which breaks down to arylamine, nitrogen and sulfuric acid.

2. The proposed mechanism was confirmed by the synthesis of 1-anthraquinonyltriazene-3-sulfonate by condensation of 1-diazoanthraquinone with sulfamic acid and by the susceptibility of this triazene to facile breakdown to 1-aminoanthraquinone, nitrogen and sulfuric acid.

3. It is suggested that the greater stability of 1-anthraquinonyltriazene-N-sulfonate in relation to its benzenoid analogs is due to the circumstance that the labile hydrogen of the triazene group is located at the nitrogen adjacent to the anthraquinonyl residue and forms a hydrogen bond with the carbonyl group of anthraquinone.

4. The location of the labile hydrogen at the nitrogen adjacent to the anthraquinonyl residue is proven by the breakdown of 1-anthraquinonyltriazene-3-sulfonate to aminoanthraquinone, nitrogen and sulfur trioxide, as well as by the formation of 1-methylaminoanthraquinone on breakdown of the product of methylation of this triazene.

5. It was found that 1-anthraquinonyl-3-sulfonate readily splits into 1-anthraquinonyl azide and sulfur trioxide under the action of alkali. This reaction is regarded as a nucleophilic substitution under the action of the hydroxyl ion.

6. It was established that sodium 1-anthraquinonyltriazene-3-sulfonate exists in a yellow and a red form, the first of which is the more stable.

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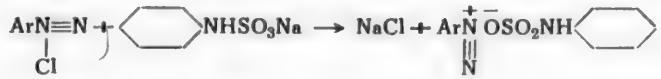
•Original Russian pagination. See C. B. Translation.

REACTIONS OF DIAZO COMPOUNDS WITH SULFAMIC ACID AND ITS DERIVATIVES

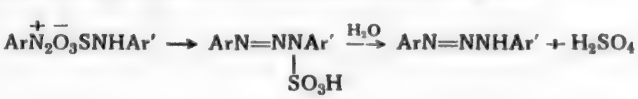
VIII. DIAZONIUM SALTS OF ARYLSULFAMIC ACIDS

D. Z. Zavel'skii and L. A. Lishnevskaia

In the preceding communication [1] we pointed out that salts of diazo compounds in aqueous solutions with a pH of 2 to 5 enter into exchange reaction with sodium benzenesulfamate with formation of aryldiazonium benzenesulfamates.



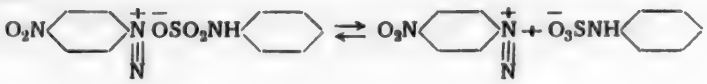
These salts later rearrange gradually, especially when the pH of the reaction medium is increased, to the unstable diaryltriazene-N-sulfonic acids which cannot be isolated due to their tendency to split off the labile sulfo group attached to the nitrogen with formation of diaryltriazenes.



It was found that benzenediazonium sulfamates differ from the majority of known diazonium salts in being deeply colored. For example the mixing of colorless solutions of 4-nitrobenzenediazonium chloride and sodium benzenesulfamate at a pH of 2 to 5 results in the reaction mass becoming deep brownish-red and in rapid deposition of deep reddish-brown, lustrous crystals. The latter were moderately soluble in water with a neutral reaction and could be recrystallized from 10% acetic acid. They are poorly soluble (with decomposition) in organic media; in the dry state they deflagrate on heating; they are stable when kept for 3–5 days, after which they darken, split off sulfuric acid and develop an odor of phenol.

An aqueous solution of the brownish crystals couples in a neutral medium with azo components (H-acid, P-salt) with formation of dyes identical with those obtained on coupling of these azo components with 4-nitrobenzenediazonium. In an acid medium it absorbs nitrites, indicating that it contains benzenesulfamic acid. Qualitative analysis showed that the compound contains exactly equivalent quantities of 4-nitrobenzenediazonium and benzenesulfamic acid. No ash remains on combustion. These properties and the elemental composition confirmed that the investigated product was the 4-nitrobenzenediazonium salt of benzenesulfamic acid.

Well-formed and deeply colored crystals of diazonium salts of benzenesulfamic acid are also formed by many other diazo compounds on reaction with benzenesulfamic acid, the products easily coming down from water. In properties they closely resemble the above-described 4-nitrobenzenediazonium salt. It is interesting that saturated solutions of all of these colored salts, which are also fairly deeply colored, become weak-yellow when diluted. We can therefore infer that the colored benzenediazonium sulfamates again form colorless ions on dissociation in water.

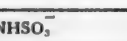
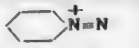
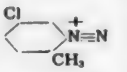
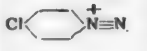
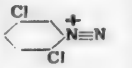
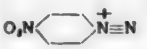
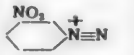
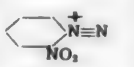
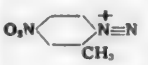
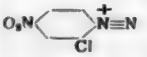
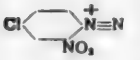
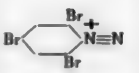


It is well-known that in the solid form the sulfates and arylsulfonates of the same diazo compounds are colorless or faint-yellow. The unusual properties of the benzenesulfamates therefore prompted us to synthesize a series of salts from diazo compounds of the benzene series and two arylsulfamic acids in order to establish how their color and some other properties change in dependence on the character and number of substituents in both of the benzene rings.

Diazochlorides were synthesized from 12 amines: aniline, 4-toluidine, 4-anisidine, 2-methyl-5-chloroaniline, 4-chloroaniline, 2,5-dichloroaniline, 4-nitroaniline, 3-nitroaniline, 2-nitroaniline, 2-methyl-4-nitro-

TABLE 1

Characteristics of Products of Reaction of Diazonium Chlorides with Sodium Salts of Arylsulfamic Acids

Preparation No.	Structure of diazonium	Structure of arylsulfamate anion	
			
1		Yellow solution. No precipitate.	Yellow solution. No precipitate.
2		Yellow-orange solution. No precipitate formed.	Yellow-orange solution. No precipitate formed.
3		Brown-orange solution. No precipitate.	–
4		Orange solution. No precipitate.	–
5		Diazonium salt. Large, golden, scaley plates.	Diazonium salt. Large, lustrous, bright orange-red plates.
6		Diazonium salt. Large bright-red needles.	Brown-red reaction mixture deposits the diazoamino compound slightly contaminated with diazonium salt which could not be isolated pure.
7		Diazonium salt. Large, lustrous, red-brown plates.	Diazonium salt. Very dark violet-brown, long plates.
8		Diazonium salt. Bright-orange plates with tapered corners.	Diazonium salt. Large, lustrous, red plates.
9		Diazonium salt hardly comes down from dark red-brown reaction mass.	Diazonium salt. Large, elongated, very dark-claret plates.
10		Diazonium salt. Large, brown prisms with pointed ends.	Diazonium salt. Lustrous, dark-brown (violet tinge), stout prisms.
11		Chocolate-colored diazonium salt comes down from the dark-brown solution and slowly changes into the diazoamino compound.	Diazonium salt. Black, elongated plates with a violet tinge. Unstable, easily changing into the diazoamino compound.
12		Diazonium salt. Claret-brown plates. Unstable. Easily change to the diazoamino compound.	Diazonium salt. Chocolate-brown elongated plates. The salt is unstable but slightly more stable than the benzenesulfamate.
13		Diazoamino compound containing only traces of diazonium salt comes down from the red-brown reaction mixture.	A mixture of diazonium salt and diazoamino compound comes down from the brown reaction mixture. The pure diazonium salt cannot be isolated.

aniline, 4-chloro-2-nitroaniline and 2,4,6-tribromoaniline. Their solutions in aqueous mineral acids were brought into reaction in the cold (after being freed from excess of nitrous acid) with sodium benzenesulfamate and sodium 4-toluenesulfamate. Results are summarized in Table 1.

The following conclusions can be drawn from the data of Table 1.

The color, solubility and stability of aryldiazonium sulfamates depend on the character of the substituents in the benzene rings of both the diazonium compounds and the arylsulfamic acids in the following manner: when the benzenediazonium ring does not contain a substituent or contains electron-donating substituents (H, 4-CH_3, 4-OCH_3) or one electron-donating and a second, relatively weakly electron-accepting, substituent (2-CH_3, 5-Cl), the resulting arylsulfamates are weakly colored, very easily soluble in water and free from a susceptibility to rearrange into triazenes.

If the substituents possess electron-accepting properties (4-Cl, 4-NO_2, 3-NO_2, 2-NO_2, 4,2-NO_2, CH_3), then the arylsulfamates are the more deeply colored the more electrophilic is the substituent in character or by virtue of its position; their solubility decreases to such an extent that they readily crystallize from solution (an exception is the deeply colored but highly soluble 2-nitrobenzenediazonium benzenesulfamate), while the tendency to rearrange into diazoamino compounds already becomes perceptible [1]. Finally, if the benzenediazonium ring contains two or three electron-accepting substituents (2,4-Cl, NO_2; 2,4-NO_2, Cl; 2,4,6-tribromo), then the arylsulfamates are even more deeply colored and so unstable that even in a mineral acid medium they rapidly rearrange to triazenes. The connecting link between the two latter groups of diazonium compounds is 2,5-dichlorobenzenediazonium, which with benzenesulfamic acid still forms quite a stable salt, whereas with toluenesulfamic acid it already mainly forms a diazoamino compound.

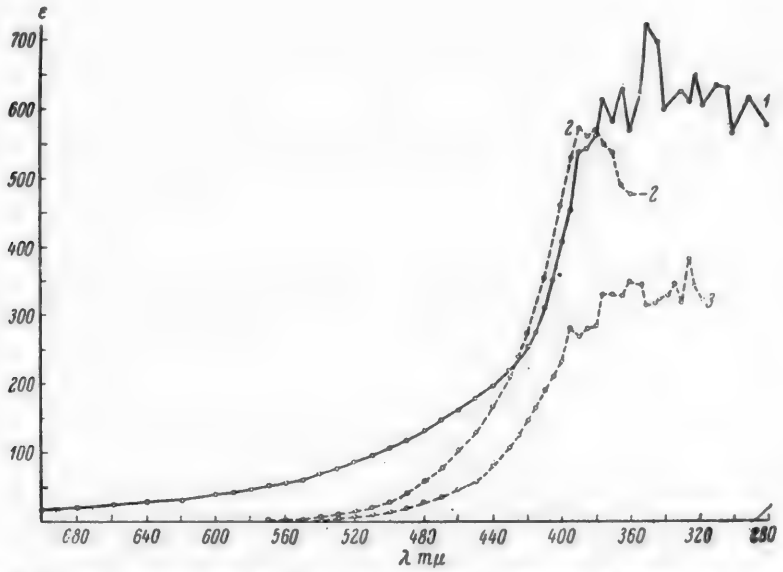


Fig. 1. Absorption spectra of 4-nitrobenzenediazonium salts of benzenesulfamic acid. 1)Aqueous saturated solution; 2) the same in 4-fold dilution; 3) the same in 10-fold dilution.

Whereas the presence of electron-donating groups in the benzenediazonium ring heightens the color of their arylsulfamates, the introduction of a methyl group into the 4-position of benzenesulfamic acid leads to deepening of color. Consequently, the lower the basicity of the diazonium cation and the acidity of the arylsulfamate anion, the more deeply colored are the salts formed by them.

It has already been remarked that although arylsulfamates of negatively substituted aryldiazoniums have very deep colors, their aqueous solutions (even when saturated) are more weakly colored. For example, solid 4-nitrobenzenediazonium benzenesulfamate forms deeply colored, red-brown crystals; its saturated solution (0.0775 M) has the color of tea, and more dilute solutions are light-yellow.

In order to obtain a closer insight into the properties of diazo compounds of arylsulfamates as colored substances, absorption spectra of aqueous solutions of four diazo salts of this series were obtained: 4-nitrobenzenediazonium benzenesulfamate and 4-toluenesulfamate, and 4-chlorobenzenediazonium benzenesulfamate and 4-toluenesulfamate (Figs. 1–4). Tables 2 and 3 contain the main numerical data characterizing the change of the molecular absorption coefficient ϵ with the concentration of aqueous solutions of the aryldiazonium sulfamates in the visible region of the spectrum.

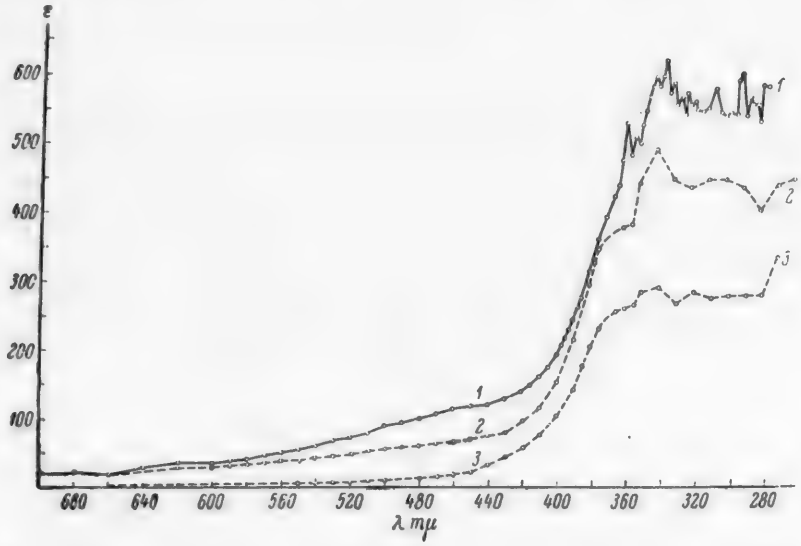


Fig. 2. Absorption spectra of 4-nitrobenzenediazonium salts of 4-toluenesulfamic acid. 1) Aqueous saturated solution; 2) the same in 4-fold dilution; 3) the same in 10-fold dilution.

We see from Figs. 1–4 that for all of the solutions of diazo salts (I) and (II), the absorption maximum is in the ultraviolet region of the spectrum (λ_{max} 340–360 mμ). For saturated solutions of the diazo compounds (III) and (IV) λ_{max} is 440 mμ, while for dilute solutions the maximum is shifted into the ultraviolet region of the spectrum.

TABLE 2

Change of ϵ with the Concentration of Aqueous Solutions of 4-Nitrobenzenediazonium Arylsulfamates

λ mμ	O_2N–C$_6$H$_4$–N_2^+ OSO_2NH–C$_6$H$_5$ (I)					O_2N–C$_6$H$_4$–N_2^+ OSO_2NH–C$_6$H$_4$–CH_3 (II)				
	ϵ_1	ϵ_4	ϵ_{10}	$\frac{\epsilon_1}{\epsilon_4}$	$\frac{\epsilon_1}{\epsilon_{10}}$	ϵ_1	ϵ_4	ϵ_{10}	$\frac{\epsilon_1}{\epsilon_4}$	$\frac{\epsilon_1}{\epsilon_{10}}$
680	22	—	—	—	—	21	20	—	1.0	—
620	34	—	—	—	—	33	26	2.2	1.27	15.0
560	57	2.1	2.0	27.00	28.5	49	37	2.7	1.33	18.2
500	108	31	15	3.50	7.2	87	55	8.6	1.58	10.1
450	179	132	62	1.36	2.9	116	68	19.3	1.70	6.0
400	409	460	233	0.89	1.8	190	149	100	1.28	1.9

Notes. ϵ_1 is here and later the molar coefficient of absorption for the saturated solution; ϵ_4 is the coefficient in 4-fold dilution, and ϵ_{10} is the coefficient in 10-fold dilution. The molar concentration of the saturated solution (I) is 0.07757 M; the molar concentration of saturated solution (II) is 0.0893 M.

TABLE 3

Change of ϵ with the Concentration of Aqueous Solutions of 4-Chlorobenzenediazonium Arylsulfamates

λ mμ	Cl⟨⟩N₂ ⁻OSO₂NH⟨⟩ (III)			Cl⟨⟩N₂ ⁻OSO₂NH⟨⟩CH₃ (IV)				
	ε_1	ε_4	$\frac{\varepsilon_1}{\varepsilon_4}$	ε_1	ε_4	ε_{10}	$\frac{\varepsilon_1}{\varepsilon_4}$	$\frac{\varepsilon_1}{\varepsilon_{10}}$
680	2.8	1.6	1.75	1.3	—	—	—	—
620	3.3	1.7	1.94	1.5	0.4	—	3.75	—
560	4.6	1.7	2.7	2.9	0.8	—	3.6	—
500	10.1	2.4	4.2	13.9	4.3	1.5	3.23	9.3
450	24.4	6.4	3.8	40.8	13.7	6.6	3.0	6.2
400	21.8	16.4	1.33	40.5	34.2	21.4	1.18	1.9

Note. The molar concentration of the saturated solution (III) is 0.2406 M; that of saturated solution (V) is 0.1279 M.

Since the solid diazo salts (I) and (II) have a very dark color, the absence of λ_{max} from the visible spectrum is evidently due to dissociation of these salts into colorless ions at a relatively low molar concentration of their saturated solutions which were used for measurements.

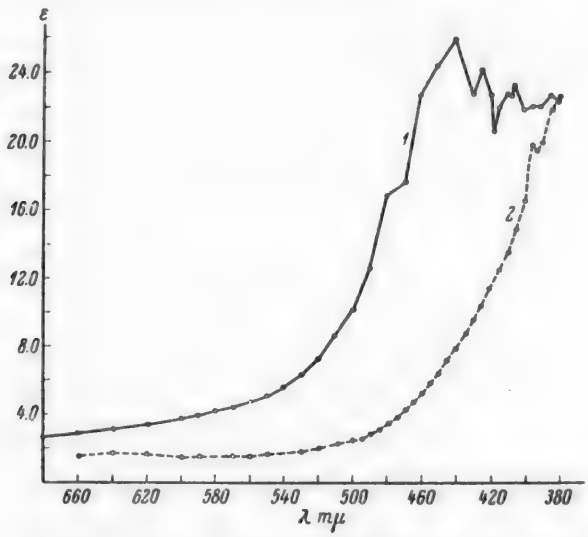


Fig. 3. Absorption spectra of 4-chlorobenzenediazonium salts of benzenesulfamic acid. 1) Aqueous saturated solution; 2) in 4-fold dilution.

Concerning diazo salts (III) and (IV), which are more highly colored in the solid form than (I) and (II), the λ_{max} of the saturated solutions is in the visible region of the spectrum, probably because their molar concentration is considerably greater than in the case of diazo salts (I) and (II).

Aqueous solutions of aryldiazonium sulfamates do not obey the Lambert-Beer law since their absorption coefficient is not proportional to the concentration.

The following conclusions can be drawn from the data of Tables 2 and 3.

1. For a saturated solution of diazo salt (I), ϵ_1 increases in the visible region from 22 at 680 mμ to 409 at 400 mμ. Such a course of the curve is characteristic of brown dyes.

2. A four-fold dilution of the saturated solution of (I) sharply reduces the molar coefficient of absorption: at 680 and 620 mμ it is difficult to measure, and at 560 mμ, ϵ_1 is 27 times greater than it. The lower the wavelength of the light the smaller the ratio of ϵ_1 to ϵ_2, so that the color of the solution approximates to yellow on dilution.

3. A 10-fold dilution of the saturated solution of (I) causes ϵ to fall even more sharply, but the ϵ_4/ϵ_{10} ratio is much smaller than ϵ_1/ϵ_4. Consequently, dissociation is already very considerable at 4-fold dilution.

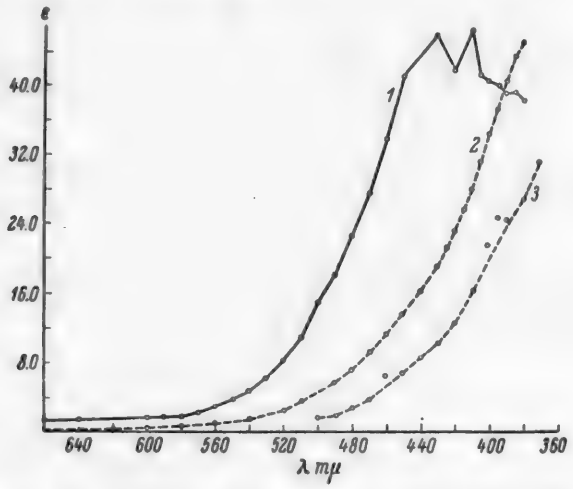


Fig. 4. Absorption spectra of 4-chlorobenzenediazonium salt of 4-toluenesulfamic acid. 1) Aqueous saturated solution; 2) the same in 4-fold dilution; 3) the same in 10-fold dilution.

4. In the case of a saturated solution of diazo salt (II), the value of ϵ_1 in the 680–500 mμ region is close to ϵ_1 of the benzenesulfamate, but in the 500–400 mμ region it rises very much more slowly.

5. A 4-fold dilution of a saturated solution of (II) causes a relatively insignificant fall in ϵ. Very much stronger dissociation is observed on 10-fold dilution (see ϵ_1/ϵ_{10} ratio in comparison with ϵ_1/ϵ_4 ratio).

6. In the case of saturated solutions of diazo salts (III) and (IV) the character of the absorption curves is little different from that of the curves of the corresponding solutions of (I) and (II), but the absolute value of ϵ for (I) and (II) is 5-20 times greater than for (III) and (IV).

7. For solutions of diazo salts (III) and (IV) diluted 4 times, the ϵ_1/ϵ_4 ratio characterizing the degree of dissociation of the diazo salts is slightly higher than for the corresponding solutions of the diazo salt (II) but considerably smaller than for diazo salt (I).

Consequently, the study of the absorption spectra of aryldiazonium sulfamates confirms the statement that the color characteristics of the latter are due to formation of undissociated salts. Dissolution of these salts and dilution of their solutions leads to dissociation of the colored salts into colorless cations and anions. The degree of dissociation evidently depends on the nature of the cation and anion of the salt.

EXPERIMENTAL

Synthesis of starting preparations. Sodium benzenesulfamate and sodium toluenesulfamate were prepared by the method described in [2] for benzenedisulfamic acid. 150 g of chlorosulfonic acid was gradually charged

into 600 g of pyridine at -5 to 0°; this was followed, at a temperature not higher than 20°, by 93 g of aniline or 107 g of 4-toluidine. The mixture was heated to 60–70°, stirred for 2 hours, and (after cooling) neutralized with sodium carbonate solution. The pyridine was distilled off with steam and the solution was evaporated on a water bath and dried in a thermostat. The resulting powder was extracted with alcohol to eliminate inorganic salts. When the alcoholic solution was cooled it deposited sodium arylsulfamate in 88–96% purity, which was raised to 99.5–99.8% by two recrystallizations from alcohol. • The yield of arylsulfamates before recrystallization was about 80% of the theoretical on the basis of the original arylamine.

A solution of diazo compound was prepared by stirring of 0.01 mole of amine with 6 ml of 5 N hydrochloric acid at room temperature for half an hour, followed by addition of 7 g of crushed ice and (in one portion) 2.1 ml of 5 N sodium nitrite solution. The resulting diazo solution was filtered and the excess of nitrous acid was removed with a few drops of sulfamic acid solution, using as an indicator paper impregnated with methyl yellow solution. In the case of weakly basic amines (4-nitro-2-chloroaniline, 2,5-dichloroaniline, etc.) the hydrochloric acid proportion was 0.05 mole per 0.01 mole of amine, and the amount of nitrite was in 10% excess over the theoretical.

When it was necessary to obtain more concentrated diazo solutions, ice was not added to the mixture of amine and hydrochloric acid, its place being taken by external cooling with ice and salt.

Synthesis of diazonium salts of arylsulfamic acids. The sodium salt of the arylsulfamic acid was dissolved at 40–50° in 4 to 5 times as much water and then cooled externally with ice. The greater part of the salt came down. A little acetic acid was added to the suspension of arylsulfamate before the diazo solution was run in in order to bring the pH to 3.5–4.0.

4-Nitrobenzenediazonium benzenesulfamate. Addition of the diazo solution to the suspension of sodium benzenesulfamate resulted in the reaction mixture acquiring a brownish-red color, and in the disappearance of the white benzenesulfamate. The solution almost immediately started to deposit lustrous, large, brownish-red crystals which have the form of plates under the microscope. The precipitated 4-nitrobenzenediazonium arylsulfamate was nearly pure after filtration, washing with ether and drying in vacuo over potassium hydroxide. Yield about 87% of the theoretical.

For the purpose of analysis the product was recrystallized from 10% acetic acid heated to 50–55°. The red-brown crystals are soluble in cold water with formation of a pale-yellowish solution. The diazo salt easily dissolves in alcohol and glacial acetic acid and in so doing undergoes extensive decomposition.

When an attempt was made to dry the substance in a thermostat or by holding a sample on the tip of a spatula on an electric hotplate, it suddenly swelled up with evolution of gas and formation of a dark-grey, porous, carbonaceous mass.

Prior to recrystallization the diazo salt was stable in storage for 1.5 to 2 days, and after recrystallization for 4 to 6 days. After this period it darkened and developed a phenolic odor, while its aqueous solution was found to contain sulfuric acid. When kept for a longer period, the diazo salt changes into a dark amorphous mass no longer giving the reactions for an active diazo compound.

Analysis of the Diazonium Salt

Ash. A weighed sample of the substance was wetted with sulfuric acid in a crucible, carefully evaporated and ignited. No ash was detected.

Nitrogen (Dumas). Diazo salts are explosive. Combustion was therefore effected in a small boat of sheet copper 20 cm long and oxidized in the flame of a gas burner. The weighed sample of diazo salt was spread out in the boat in small portions which were separated by layers of fine copper oxide.

Found %: N 17.21, 17.35. $C_{12}H_{10}O_5N_4S$. Calculated %: N 17.39.

Diazo nitrogen. The sample of diazo salt was heated in 50% sulfuric acid. The liberated nitrogen was collected over potassium hydroxide solution.

• The arylsulfamic acids could be analyzed by titration with nitrite in hydrochloric acid solution in presence of potassium bromide.

Found %: diazo nitrogen 8.61. $C_{12}H_{10}O_6N_4S$. Calculated %: diazo nitrogen 8.69.

Diazo cation. A weighed sample of diazo salt was dissolved in 150–200 ml of water and an excess of neutral standard solution of β-naphthol was added. The pH was brought to 7 by addition of bicarbonate, and after 30 minutes the excess of β-naphthol was determined by titration with a p-nitrobenzenediazonium solution.

0.5228 g of substance. Found: consumption of 0.1 N β-naphthol 15.95 ml. $C_{12}H_{10}O_6N_4S$. Calculated: consumption of β-naphthol 16.20 ml.

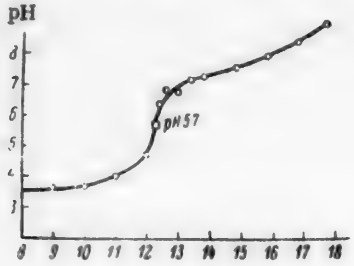


Fig. 5. Potentiometric titration curve of the 4-nitrobenzenediazonium salt of benzenesulfamic acid.

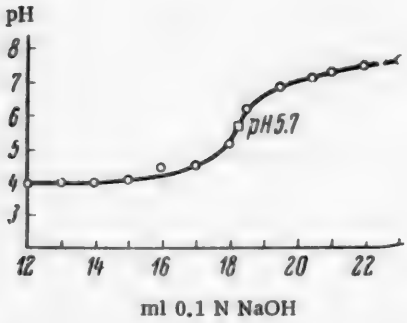


Fig. 6. Potentiometric titration curve of the 4-nitrobenzenediazonium salt of 4-toluenesulfamic acid.

Benzenesulfamate anion. The reaction mixture obtained after determination of the diazo cation was filtered from the β-naphthol azo dye. The filtrate and wash liquors were acidified with 25 ml of concentrated hydrochloric acid, 0.5 g of potassium bromide was added, and the benzenesulfamic acid was back-titrated with nitrite.

0.5228 g of substance: consumption of 0.1 N $NaNO_2$ 15.9 ml. $C_{12}H_{10}O_6N_4S$. Calculated: consumption of 0.1 N $NaNO_2$ 16.2 ml.

Potentiometric titration of the diazo salt. A weighed sample of the substance was dissolved in water, a small quantity of 0.1 N HCl was added, and the solution was titrated with 0.1 N NaOH, using a glass electrode (in the State Institute of Applied Chemistry type of pH-meter). The isoelectric point was found to lie at pH 5.7.

4-Nitrobenzenediazonium salt of 4-toluenesulfamic acid. After the diazo solution had been run into a suspension of sodium toluenesulfamate in water, the reaction mixture at once acquired a dark-brown color. A dark precipitate came down after a few minutes. It was filtered and recrystallized from water heated to 50–55°. Deeply colored violet-brown crystals were obtained with the appearance of elongated plates under the microscope. The color of the mother liquor was pale-yellow; after standing for 40 minutes it deposited a yellowish substance insoluble in water and not coupling with azo components in a neutral medium. This precipitate gave an intense coloration when heated in glacial acetic acid in presence of α-naphthylamine; it is therefore a diazoamino compound.

Found %: diazo nitrogen 8.10. $C_{12}H_{12}O_6N_4S$. Calculated %: diazo nitrogen 8.33.

Potentiometric titration of the diazo salt revealed an isoelectric point at pH 5.7.

3-Nitrobenzenediazonium salt of benzenesulfamic acid. An orange solid forming lustrous, bright-orange crystals after recrystallization from water heated to 50°. Plates with tapered corners under the microscope. The salt is soluble in cold water to give a yellowish-orange solution.

Found %: diazo nitrogen 8.40. $C_{12}H_{10}O_6N_4S$. Calculated %: diazo nitrogen 8.69.

3-Nitrobenzenediazonium salt of 4-toluenesulfamic acid. The reaction mixture turned red when the diazo solution was run into a suspension of sodium 4-toluenesulfamate, and crystallization occurred in a few minutes. The substance was recrystallized from water heated to 80° to give large, lustrous orange-red crystals; appearance of plates under the microscope.

Found %: diazo nitrogen 8.32. $C_{12}H_{12}O_6N_4S$. Calculated %: diazo nitrogen 8.33.

2-Nitrobenzenediazonium salt of benzenesulfamic acid. A diazo solution of maximum concentration and a thick suspension of sodium benzenesulfamate were reacted. After standing in the cold, only a small quantity of solid came down which after filtration had the form of a brown paste. Under the microscope it consisted of fine, poorly formed crystals. The paste was very easily soluble in water and imparted a yellow color. The solution coupled intensively with azo coupling agents. Due to the small quantity, the diazonium salt was not analyzed or purified.

2-Nitrobenzenediazonium salt of 4-toluenesulfamic acid. A concentrated solution of the diazo compound was run into a thick suspension of sodium 4-toluenesulfamate. The reaction mixture acquired a dark red-brown color. A small quantity of claret-colored solid came down after a few minutes. Stout, pale-red plates under the microscope.

Found %: diazo nitrogen 8.11. $C_{13}H_{12}O_5N_4S$. Calculated %: diazo nitrogen 8.33.

2-Methyl-4-nitrobenzenediazonium salt of benzenesulfamic acid. A precipitate came down after the cooled mixture of reactants had stood for 30 minutes. Under the microscope it consisted of stout crystals with the form of prisms with sharp ends. After recrystallization from water heated to 55°, the diazo salt acquired a claret-brown color darker than the color of 4-nitrobenzenediazonium benzenesulfamate.

Found %: diazo nitrogen 8.33. $C_{13}H_{12}O_5N_4S$. Calculated %: diazo nitrogen 8.33.

2-Methyl-4-nitrobenzenediazonium 4-toluenesulfamate. Mixing of the components led to formation of a reddish-violet viscous mass. The recrystallized product consisted of lustrous, dark-brown crystals with a violet tinge; stout prisms under the microscope.

Found %: diazo nitrogen 8.09. $C_{14}H_{14}O_5N_4S$. Calculated %: diazo nitrogen 8.00.

2-Chloro-4-nitrobenzenediazonium benzenesulfamate. The reaction mixture at once turned dark-brown and a chocolate-brown precipitate quickly came down and gradually became paler. This precipitate was only poorly soluble in water (yellow solution) and it did not couple intensively with azo components. Under the microscope it consisted of fine, poorly formed crystallites, altogether dissimilar from the stout crystals of the previously described diazo salts. A sample dissolved in glacial acetic acid, to which α-naphthylamine was added, gave an intense coloration. The precipitate is therefore mainly a diazoamino compound. The pure diazonium salt of benzenesulfamic acid could not be isolated from the solid. This signifies that even in a mineral acid medium, 2-chloro-4-nitrobenzenediazonium at first forms a salt with benzenesulfamic acid and the salt rapidly changes into the insoluble diazoamino compound.

2-Chloro-4-nitrobenzenediazonium 4-toluenesulfamate. The nearly black (with violet-brown tinge) reaction mixture deposited after 2–3 minutes a thick slurry of violet-black crystals with the appearance of elongated plates under the microscope. It was rapidly filtered; the product was completely soluble in water (weak-yellow color) and intensively coupled with azo components, but it could not be recrystallized or even dried without decomposition. A few minutes after it had been separated from the mother liquor and washed with glacial acetic acid, the compound began to darken and at the same time lost its solubility in water. It quickly changed into a brownish-yellow compound, insoluble in water and not coupling with azo components in a neutral medium. The new substance dissolved in glacial acetic acid with an orange color, and addition of α-naphthylamine to the solution gave a bright coloration characteristic of diazoamino compounds.

4-Chlorobenzenediazonium benzenesulfamate. A saturated solution of sodium chloride was added to the reaction mixture which was cooled with ice. Stout, golden scales came down (plates under the microscope). The product was recrystallized from water heated to 70–80°. The golden-yellow crystals were filtered, washed with iced water, pressed on porous porcelain and dried in vacuo over solid potassium hydroxide. The color of the aqueous solution of the salt varies from yellow to colorless in dependence on the concentration.

Found %: diazo nitrogen 8.95. $C_{12}H_{10}O_3N_3SCl$. Calculated %: diazo nitrogen 8.98.

4-Chlorobenzenediazonium 4-toluenesulfamate. The reaction solution turned red, and after a few minutes it deposited red crystals (stout plates under the microscope). Recrystallization gave stout, lustrous, orange-red plates. The color of the aqueous solution of the salt varied from yellow-orange to colorless in dependence on the concentration.

Found %: diazo nitrogen 8.57. $C_{13}H_{12}O_3N_3SCl$. Calculated %: diazo nitrogen 8.60.

2,5-Dichlorobenzenediazonium benzenesulfamate. After 2–3 minutes the reaction solution deposited a thick slurry of bright-red crystals. With the objective of recrystallization, the filtered precipitate was ground into a paste with 10% acetic acid solution and then dissolved in water heated to 65-70°. Stout red crystals came down after cooling, and had the appearance of needles under the microscope. The solid was washed with ether on the filter, pressed on porous porcelain and dried in vacuo. The color of the aqueous solution of the salt varied from reddish-orange to pale-yellow in dependence on the concentration.

Found %: diazo nitrogen 7.87. $C_{12}H_9O_3N_3SCl_2$. Calculated %: diazo nitrogen 8.09.

2,5-Dichlorobenzenediazonium 4-toluenesulfamate. The brown-red reaction solution gradually deposited a light-brown solid poorly soluble in water and coupling weakly with azo components. Solution of the product in glacial acetic acid, addition of α-naphthylamine and gentle heating led to development of a bright violet color. The precipitate in the main therefore consisted of the diazoamino compound.

4-Chloro-2-nitrobenzenediazonium benzenesulfamate. The reddish-brown reaction mixture crystallized after 2–3 minutes. The filtered precipitate consisted of claret-brown crystals (elongated plates under the microscope). The product was nearly completely soluble in cold water to form a pale-yellow solution, and it actively coupled with diazo components. The salt was extremely unstable. It changed partly into diazoamino compound on recrystallization or drying.

4-Chloro-2-nitrobenzenediazonium 4-toluenesulfamate. After a few minutes the reaction solution deposited a chocolate-brown substance (elongated plates under the microscope). After washing with iced water, pressing on porous porcelain and drying in vacuo, the product nearly completely retained its azo-coupling ability. On recrystallization from water it was partially converted into the diazoamino compound.

2,4,6-Tribromobenzenediazonium benzenesulfamate. After 2,4,6-tribromodiazobenzene had been run into a suspension of sodium benzenesulfamate, the reaction mixture at first was colored red-brown, but quickly lightened and deposited a yellow-brown solid which was poorly soluble in water and coupled weakly with azo components. It formed an azo dye with α-naphthylamine. The diazo salt is accordingly already converted into the diazoamino compound in the mineral acid reaction solution.

2,4,6-Tribromobenzenediazonium 4-toluenesulfamate. The reaction mixture acquired an orange-brown color when a concentrated diazo solution was run into the thick suspension of toluenesulfamate. A small precipitate came down after a few minutes. The quantity was not increased by salting-out and cooling. The orange-yellow, filtered product only dissolved partly in water and coupled weakly with azo components. Two forms of crystals were observed under the microscope: small but well-formed plates (probably diazo salt) and very fine crystallites of indeterminate structure, sticking to the plates. The pure diazo salt could not be isolated from the precipitate.

Benzenediazonium chloride and sodium benzenesulfamate. A yellow solution was formed when a solution of benzenediazonium chloride of maximum concentration was run into a thick suspension of sodium benzenesulfamate. No precipitate could be obtained by cooling, by salting-out with sodium chloride or sodium sulfate, etc.

4-Toluenediazonium chloride, 4-methoxybenzenediazonium chloride and 5-chlorobenzenediazonium chloride form yellow to orange solutions with sodium benzenesulfamate from which no precipitate could be obtained. Similar results were obtained with benzenediazonium chloride and 4-toluenediazonium chloride on the one hand and sodium toluenesulfamate on the other.

Measurement of the absorption spectra of aqueous solutions of aryldiazonium sulfamates. Saturated aqueous solutions of the following diazo salts were prepared: a) 0.07757 M 4-nitrobenzenediazonium benzenesulfamate; b) 0.08903 M 4-nitrobenzenediazonium 4-toluenesulfamate; c) 0.2406 M 4-chlorobenzenediazonium benzenesulfamate; d) 0.1279 M 4-chlorobenzenediazonium benzenesulfamate.

Each of the saturated solutions was diluted 4-fold and 10-fold with water. The absorption spectra of the solutions were measured with the SF-4 spectrophotometer. The optical density D was determined at wavelengths of 700 to 380–280 mμ. The molecular coefficient of absorption was calculated from the formula

$$\varepsilon = \frac{1}{B \cdot C} \cdot 2.3\,D,$$

where B is the thickness of the solution layer in centimeters and C is the molar concentration per liter. Aqueous solutions of aryldiazonium sulfamates have poor stability. Solutions must therefore be frequently replaced by fresh ones during the measurements.

SUMMARY

1. Deeply colored salts ranging in color from yellow and orange to nearly black are formed by reaction of arylsulfamic acids with aryldiazonium compounds containing electron-accepting substituents.

2. It was shown that the more electronegative the substituents in the aryldiazonium cation are the deeper the color of the resulting salt of arylsulfamic acid will be. Such an effect is induced by electron-donating substituents in the arylsulfamic acid.

3. In water the aryldiazonium sulfamates form saturated solutions that are very much more colored than the solid salts. They lose their color on dilution and accordingly do not obey the Lambert-Beer law.

4. It was shown that the color characteristics of aryldiazonium sulfamates are caused by the formation of undissociated salts by these components. The loss of color of aqueous solutions of aryldiazonium sulfamates on dilution is a consequence of their dissociation into colorless cations and anions.

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INVESTIGATIONS ON THIOSULFONIC ACIDS

III. ALKYL ESTERS OF PHENYLMETHANE THIOSULFONIC ACID AND THEIR ANTIBACTERIAL PROPERTIES

B. G. Boldyrev and Iu. I. Kofman

In the preceding communications [1,2] on the properties of alkyl esters (I) of alkanethiosulfonic acids obtained by one of us with co-workers, we observed that the antibacterial activity of these compounds does not depend upon the size and structure of the radicals on the side of the oxide sulfur and substantially remains constant for esters of thiosulfonic acids of both normal and isostructures with 1 to 4 carbon atoms.

$$\underset{\text{(I)}}{Alk-SO_2-S-Alk'} \qquad \underset{\text{(II)}}{C_6H_5-CH_2-SO_2-S-Alk}$$

For this reason we decided in the present work to synthesize and study the properties of alkyl esters (II) of phenylmethanethiosulfonic acid in order to establish the influence of change of character of the radicals of thiosulfonic acids on the antibacterial activity of the esters.

We synthesized alkyl esters of phenylmethanethiosulfonic acid by our previously described method [1]; the esters prepared are listed in the table. They are colorless, crystalline substances with a weak specific odor, readily soluble in alcohol, ether, acetone and other organic solvents, poorly soluble in water.

TABLE

Alkyl Esters of Phenylmethanethiosulfonic Acid

$C_6H_5-CH_2-SO_2-S-Alk$

Preparation no	Alk	Melting point	Sulfur content (%) found	Sulfur content (%) calc.	Yield (%)	Crystal forms (from anhydrous alcohol)
1	CH_3-CH_2-	70—71°	29.88	29.80	29.3	Tetragonal prisms
2	$CH_3-CH_2-CH_2-$ . . .	44	28.02	27.84	44.4	Hexagonal prisms
3	$(CH_3)_2CH-$	61—62	27.74	27.84	21.0	Elongated hexagonal prisms
4	$CH_2=CH-CH_2-$ . . .	27	27.95, 28.02	28.09	33.8	From 40% alcohol: crystals of indeterminate form
5	$CH_3-CH_2-CH_2-CH_2-$	34—35	26.17	26.24	37.0	Elongated thin needles
6	$(CH_3)_2CH-CH_2-$ . . .	44—45	26.10, 26.30	26.24	22.0	Elongated thin needles

A study of the antibacterial properties of the esters (II), carried out by the Institute of Microbiology of the Academy of Sciences of the Ukrainian SSR, showed that the activity of these compounds towards gram-positive, gram-negative and acid-resistant bacteria is lower than that of alkyl esters of alkanethiosulfonic acids

containing 1 to 4 carbon atoms; at the same time the activity of esters (II) towards various fungi increases to a considerable degree.

The present work thus showed that the antibacterial properties of esters of thiosulfonic acids depend not only on the character of the radicals linked to the sulfide sulfur but also on the structure of the original thiosulfonic acids.

EXPERIMENTAL

The intermediates for synthesis of esters (II)—sodium phenylmethanesulfonate and phenylmethanesulfochloride—were prepared by the literature methods [3,4].

Potassium phenylmethanethiosulfonate, not previously described, was synthesized in a similar manner to other alkanethiosulfonates [1,2]. It is a colorless, crystalline substance with m.p. 220–221°, readily soluble in water, more difficultly soluble in boiling alcohols, insoluble in ether, acetone, benzene and other organic solvents. The potassium salt crystallizes from ethyl alcohol in the form of slender, rectangular plates; from butyl alcohol it crystallizes as extremely thin, square crystals.

Found %: S 28.16. $C_7H_7O_2S_2K$. Calculated %: S 28.33.

Alkyl esters of phenylmethanethiosulfonic acid were prepared as in the preceding papers [1,2]. They were usually isolated in the form of colored, oily liquids which crystallized with difficulty in a freezing mixture and required numerous recrystallizations from 40% alcohol; this also accounts for the low yields of pure products. The quantity of acetone influences the purity of the end products; when used in the proportion of less than 100 ml per 20 g of thiosulfonate, the products are more strongly colored. Removal of acetone from the reaction mass was effected by suction at room temperature in vacuo, since evaporation on a water bath led to more deeply colored and very difficultly crystallizable products.

SUMMARY

1. Potassium phenylmethanethiosulfonate and 6 alkyl esters of phenylmethanethiosulfonic acid, not previously described, were synthesized.

2. The antibacterial properties of esters of phenylmethanethiosulfonic acid were studied; data for these compounds showed that the antibacterial activity of esters of thiosulfonic acids depends not only on the character of the radicals attached to the sulfide sulfur but also on the structure of the original thiosulfonic acids.

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THE REACTION OF ALLYLOXYETHANOL WITH VINYL ETHERS

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The investigations carried out by M. F. Shostakovskii et al. [1] on a large number of individual syntheses demonstrated the possibility of preparing acetals by reacting vinyl ethers with hydroxyl-containing compounds. In particular, they described the synthesis of acetals containing an unsaturated radical [2].

The present investigation was undertaken to prepare acetals based on allyloxyethanol and to examine their capacity for copolymerization.

These acetals were synthesized by M. F. Shostakovskii's method [1] from vinyl ethers and allyloxyethanol.

$$CH_2{=}CHOR + CH_2{=}CHCH_2OCH_2CH_2OH \longrightarrow CH_3CH\begin{matrix}OR\\ OCH_2CH_2OCH_2CH{=}CH_2\end{matrix}$$

where: R = C_2H_5, iso-C_3H_7, n-C_4H_9.

It is known [3] that the acetals of allyl alcohol (diallylformal, ethylal, butyral) are incapable of polymerization by a radical or ionic mechanism, but readily form copolymers with a lattice structure with polar monomers (vinyl acetate, acrylates, etc.).

We investigated the capacity of allyloxyethanol acetals for copolymerization with methyl methacrylate in a ratio of 10 : 90 in the presence of benzoyl peroxide. In all cases solid, colorless, transparent polymers were obtained; some of them had a higher thermostability than poly-(methyl methacrylate).

EXPERIMENTAL

As starting materials we used allyloxyethanol, prepared by the method we developed previously [4], and vinyl ethers, which were kindly given to us by M. F. Shostakovskii. The constants of the starting materials corresponded to literature data [1].

On distilling the acetals obtained as a result of disproportionation, we obtained three main fractions: 1st fraction—the symmetrical, low-boiling acetal, which corresponded to literature data [2] in its constants; 2nd—the unsymmetrical acetal and the 3rd fraction was the same in all cases and consisted of diallyloxyethyl acetal. The constants and the analysis results of the acetals obtained are given in Table 1.

Ethyl allyloxyethyl acetal. 36 g of vinyl ethyl ether and 51 g of allyloxyethanol were used. We obtained 15.4 g of diethyl acetal (b.p. 102–104°), 59.8 g of ethyl allyloxyethyl acetal and 7.6 g of diallyloxyethyl acetal.

Isopropyl allyloxyethyl acetal. 27.7 g of vinyl isopropyl ether and 32.8 g of allyloxyethanol were used. We obtained 8.2 g of diisopropyl acetal (b.p. 45–46° at 15 mm), 35.5 g of isopropyl allyloxyethyl acetal and 13.62 g of diallyloxyethyl acetal.

n-Butyl allyloxyethyl acetal. 18.3 g of vinyl n-butyl ether and 18.4 g of allyloxyethanol were used. We obtained 6.3 g of dibutyl acetal (b.p. 184–186°), 14.2 g of butyl allyloxyethyl acetal and 7.6 g of diallyloxyethyl acetal.

TABLE 1

Allyloxyethanol Acetals of the Type $CH_3CH\langle^{OR}_{OCH_2CH_2OCH_2CH=CH_2}$

Name of acetal	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	% C found	% C calc.	% H found	% H calc.	M found	M calc.
Ethyl allyloxyethyl acetal	82— 83° (15)	0.9146	1.4163	48.0	48.22	61.10, 62.19	62.0	10.31, 10.35	10.40	171.2, 170.6	174
Isopropyl allyloxyethyl acetal	87— 89° (15)	0.9013	1.4192	52.77	52.84	63.69, 63.71	63.80	10.54, 10.51	10.63	186.3, 185.1	188
n-Butyl allyloxyethyl acetal	110—112° (18)	0.9022	1.4257	57.42	57.47	65.13, 65.16	65.34	10.60, 10.88	10.83	199.8, 197.9	202
Diallyloxyethyl acetal	96— 98° (2)	0.9615	1.4410	63.25	63.24	62.49, 62.54	62.6	9.51, 9.53	9.56	225.2, 226.6	230

TABLE 2

Copolymers of Allyloxyethanol Acetals with Methyl Methacrylate

Name of starting acetal	Properties of copolymers: Brinell hardness (in kg/mm²)	Properties of copolymers: VIK thermostability
Ethyl allyloxyethyl acetal	11.37	78—79°
Isopropyl allyloxyethyl acetal	12.25	80—81
n-Butyl allyloxyethyl acetal	13.27	84—86
Diallyloxyethyl acetal	15.25	110—112

Copolymerization of acetals obtained with methyl methacrylate. The copolymerization was performed with the proportions 90% of methyl methacrylate and 10% of each of the acetals. The initiator was benzoyl peroxide (1% of the weight of the mixture). In all the experiments the temperature was gradually raised from 45 to 100° by 10° over equal time intervals. After 72 hours we obtained clear, colorless, solid polymers. The properties of some of them are given in Table 2.

SUMMARY

1. The previously unknown ethyl allyloxyethyl acetal, isopropyl ethylallyloxyethyl acetal, n-butyl allyloxyethyl acetal and diallyloxyethyl acetal of acetaldehyde were prepared and described.

2. Copolymerization of the acetals prepared with methyl methacrylate gave copolymers which had a higher thermostability than that of poly-(methyl methacrylate).

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THE SYNTHESIS OF PHENYLDIFLUOROACETIC ACID AND ITS DERIVATIVES

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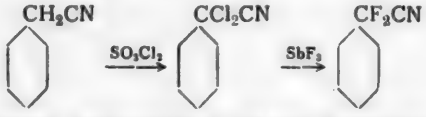
The derivatives of phenylacetic acid have been studied thoroughly as many of them are physiologically active substances with a capacity for stimulating the growth of plants [1].

We undertook the synthesis of phenyldifluoroacetic acid and its derivatives which have not been described in the literature. For this purpose we studied the reaction of phenyldichloroacetonitrile with antimony trifluoride.

As the starting material we used benzyl cyanide which was chlorinated by Claisen's method [2] with sulfuryl chloride and then fluorinated with antimony trifluoride. It was found that the cyano group was untouched and was not substituted by fluorine. The reaction proceeded by the scheme



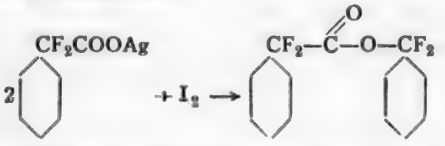
The nitrile obtained was converted to the amide in the cold by concentrated sulfuric acid. When the amide was heated with 10% sodium hydroxide it gave phenyldifluoroacetic acid.

Nitration of this acid gave m-nitrophenyldifluoroacetic acid. The position of the nitro group was determined by heating the m-nitrophenyldifluoroacetic acid in sulfuric acid (monohydrate). This gave m-nitrobenzoic acid.

Phenyldifluoroacetic and m-nitrophenyldifluoroacetic acids are quite strong acids. Their pK* values equal 2.16 and 1.89, respectively.

Reduction of m-nitrophenyldifluoroacetic acid gave the m-amino derivative. Apparently, m-aminophenyldifluoroacetic acid is an internal salt. It melted with decomposition at 235–240°, crystallized from water, was insoluble in organic solvents and soluble in solutions of soda and alkali and dissolved with difficulty in acids. m-Aminophenyldifluoroacetic acid was diazotized to give addition products.

The silver salt of phenyldifluoroacetic acid reacted peculiarly with iodine to form the ω,ω-difluorobenzyl ester of phenyldifluoroacetic acid by the scheme



The structure of the ester obtained was determined by hydrolyzing it in an acid and an alkaline medium. When heated with sulfuric acid (monohydrate) it formed benzoic acid quantitatively; when boiled with 10% sodium hydroxide it gave a mixture of benzoic and phenyldifluoroacetic acids.

* The pK was determined by potentiometric titration using a tube pH meter with a glass electrode.

We tried to alter the direction of the reaction of the silver salt of phenyldifluoroacetic acid with iodine to obtain phenyldifluoroiodomethane. For this purpose the reaction was carried out by grinding the dry components in the cold in equimolecular amounts or by heating iodine with the silver salt of phenyldifluoroacetic acid in carbon tetrachloride. The ratio of iodine to silver salt, the order of addition and the concentration of iodine in the carbon tetrachloride solution were varied. However, in all cases only ω,ω-difluorobenzyl ester of phenyldifluoroacetic acid was isolated.

EXPERIMENTAL

Phenyldichloroacetonitrile. 58 g of benzyl cyanide and 332 g of sulfuryl chloride were mixed. When the mixture had stood for a day, the excess sulfuryl chloride was distilled off at room temperature and the product vacuum distilled. The yield was 74 g (89.8%). The b.p. was 91–92° (8 mm). The product had a lachrimatory effect. A b.p. of 135° (20 mm) is reported in the literature [2].

Phenyldifluoroacetamide. 30 g of phenyldichloroacetonitrile and 34.6 g of antimony trifluoride were heated over a naked flame until a reaction began. The reaction proceeded for some time without heating. On further heating, a clear, colorless liquid distilled off at 150–160°. The product was dissolved in ether and the ether solution washed with dilute hydrochloric acid to remove antimony trichloride and then with water and dried. The ether was removed and the nitrile distilled from a flask with a pear fractionating column. A fraction was collected from 151–153°. The product was redistilled. The b.p. was 151–152°. The yield was 10 g (42%).

5 g of phenyldifluoroacetonitrile was mixed with 20 g of concentrated sulfuric acid and left overnight. The clear, colorless solution was poured onto ice. The white precipitate of amide formed was recrystallized from hot water. The yield was 4.65 g (83%) and the m.p. 114–115°.

Found %: N 8.17; F 22.05. $C_8H_7ONF_2$. Calculated %: N 8.18; F 22.22.

Phenyldifluoroacetic acid. 14.5 g of phenyldifluoroacetamide was boiled for 12 hours with 41.5 ml of 10% sodium hydroxide under reflux in a round-bottomed flask. The hydrolyzate was acidified with dilute sulfuric acid. The phenyldifluoroacetic acid precipitated as an oil. The acid was extracted with ether, the ether solution dried and the ether distilled off. The solid, crude product was recrystallized from petroleum ether (b.p. 47–50°). The yield was 12 g (82.2%). The m.p. was 76–77°. The substance formed clear, colorless needles. The acid was readily soluble in benzene, ether and methyl and ethyl alcohols.

Found %: F 21.97. $C_8H_6O_2F_2$. Calculated %: F 22.09.

Phenyldifluoroacetyl chloride. 4 g of phenyldifluoroacetic acid was boiled with 15 ml of thionyl chloride for 6 hours. The excess thionyl chloride was distilled off. The residue was vacuum distilled. The yield was 3.7 g (84%). The colorless oil had b.p. 67–68° (15 mm).

Ethyl phenyldifluoroacetate. 2.5 g of phenyldifluoroacetyl chloride was carefully added to 3 g of anhydrous ethyl alcohol. Heat was evolved during the reaction.

To complete the reaction the mixture was boiled under reflux for 30 minutes on a water bath. The excess alcohol was distilled off on a water bath and the residue vacuum distilled. The yield was 1.6 g (61.5%) and the b.p. 88–89° (9 mm). The colorless oil had a pleasant smell.

Phenyldifluoroacetanilide. Phenyldifluoroacetyl chloride was mixed with a solution of aniline in dry benzene in the cold. The yield of anilide was quantitative. The m.p. was 106–107° (from aqueous alcohol).

Found %: N 5.78. $C_{14}H_{11}ONF_2$. Calculated %: N 5.66.

m-Nitrophenyldifluoroacetic acid. Into a three-necked flask fitted with a thermometer and a stirrer was placed 3.5 ml of nitric acid (d 1.5) and 5.9 ml of sulfuric acid (d 1.83). The mixture was cooled to 0° and 4 g of phenyldifluoroacetic acid was added in portions with stirring. The temperature of the reaction mixture was kept at 20–22° and the acid added over a period of 35 minutes. The mixture was left for 1 hour at room temperature (17°) and then for another hour at 40–45°. When the reaction mixture was poured onto ice, a white crystalline precipitate formed. The precipitate was filtered off, washed with ice-water and dried. The product was recrystallized from benzene. The yield was 3.93 g (78.6%). The m.p. was 113–114°.

Found %: N 6.47. $C_8H_5O_4NF_2$. Calculated %: N 6.45.

m-Aminophenyldifluoroacetic acid. Into a reaction vessel fitted with a stirrer, a thermometer and a reflux condenser was placed 1.5 g of m-nitrophenyldifluoroacetic acid, 1.7 ml of concentrated hydrochloric acid and 1.7 ml of water. The contents of the reaction vessel were heated to 60° on a water bath and stirred, 1.5 g of iron filings was added in small portions while the temperature was gradually raised to 80°. The temperature was kept at 80° for 2 hours and then the solution was made weakly alkaline to phenolphthalein with 10% sodium hydroxide solution and filtered. The sludge was washed with a 10% sodium hydroxide solution and water. The filtrate was acidified with hydrochloric acid and evaporated on a water bath until crystallization began. The product was readily soluble in alkali and quantitatively precipitated by hydrochloric and acetic acids. It crystallized from hot water in the form of lustrous needles. The decomp. point was 235-240°. The yield was 1 g (77.5%).

Found %: F 20.17; N 7.49. $C_8H_7O_2NF_2$. Calculated %: F 20.3; N 7.48.

Silver salt of phenyldifluoroacetic acid. A solution of 5.8 g of the sodium salt of phenyldifluoroacetic acid in 20 ml of water was mixed with 5 g of silver nitrate in 10 ml of water. The salt precipitated was recrystallized from hot water. The decomp. point was 205°. The yield was 6.5 g (81.3%).

Found %: Ag 38.5. $C_8H_5O_2F_2Ag$. Calculated %: Ag 38.6.

ω,ω-Difluorobenzyl ester of phenyldifluoroacetic acid. 5.7 g of the dry silver salt and 5.7 g of ground iodine were placed in a round-bottomed flask fitted with a reflux condenser, and 25 ml of anhydrous carbon tetrachloride added. The mixture was placed on a paraffin bath and heated to 65°. At 67° a vigorous reaction began and proceeded for 10 minutes without external heating. The temperature of the bath was maintained at 67–70° for 20 minutes and then raised until the carbon tetrachloride boiled gently for 1 hour. The precipitate of silver iodide was filtered off and washed with carbon tetrachloride. The filtrate was washed free from iodine by titration with 0.1 N sodium bisulfite solution and dried. The carbon tetrachloride was distilled off on a water bath under reduced pressure provided by a water pump. A crystalline product remained. The yield was 2.7 g (90%). The clear, colorless prisms had m.p. 65.5–66° (from petroleum ether).

Found %: F 25.24. $C_{15}H_{10}O_2F_2$. Calculated %: F 25.5.

SUMMARY

The synthesis of phenyldifluoroacetic acid and its derivatives (nitrile, amide, acid chloride, ethyl ester and anilide) are described.

We prepared m-nitro- and m-aminophenyldifluoroacetic acids.

It was shown that the silver salt of phenyldifluoroacetic acid reacts with iodine to form the ω,ω-difluorobenzyl ester of phenyldifluoroacetic acid.

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SYNTHESIS AND INVESTIGATION OF POLY-3,3'-DIMETHYL-DIPHENYLMETHANEADIPO-N,N'-DIETHYLAMIDE

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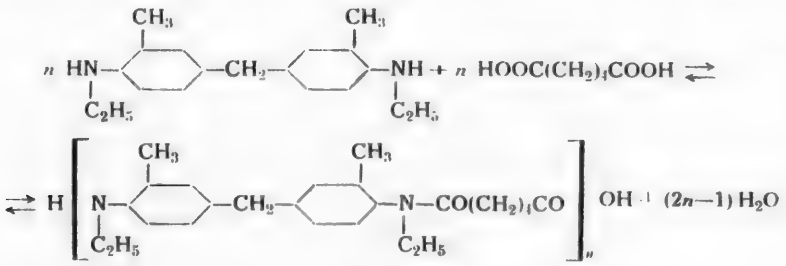
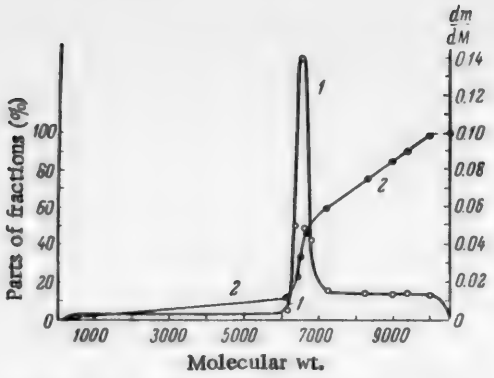
In one of our earlier papers [1] we examined some of the characteristics of the synthesis and properties of poly-3,3'-dimethyldiphenylmethaneadipamide. It was noted that this product is very hard, high-melting and insoluble in the usual organic solvents. Wishing to study the effect of substitution on the nitrogen and to obtain polymers soluble in ordinary solvents, in the present work we turned our attention to one of the most widely used methods of modifying polyamides, namely to the use of N-alkylated diamines. For this purpose N,N'-diethyl-4,4'-diamino-3,3'-dimethyldiphenylmethane [2], which reacts with adipic acid in the following way, was taken:



From this polycondensation a low-melting, brittle, glass-like product was obtained, of pale yellow color, soluble in the lower alcohols, acetone, benzene, formic and acetic acids, tricresol etc. The specific viscosity of a 0.5% solution of the polyamide in methanol was 0.09–0.13, which, with $K_m = 10.45 \cdot 10^{-4}$, corresponds to molecular weights of 9,000–12,000. We determined the value of K_m used by the light-scattering method; a similar result (K_m $10.75 \cdot 10^{-4}$) was obtained by chemical determination of end groups.

A series of experiments enabled us to determine the optimum conditions for the synthesis of the polyamide, which in general outline was as follows: the highest molecular weight polymer is obtained by carrying out the reaction in a stream of inert gas for 5 hours and then in vacuum (3–5 mm) at 240–260°. The use of vacuum for completing the reaction enables the molecular weight of the polyamide to be increased from 5,500–6,500 to 9,050–9,330.

It is known that aromatic diamines in contrast to diamines of the aliphatic series do not give salts with dicarboxylic acids [3]; this hinders to a marked extent the maintenance of the equimolecular relationship of the initial substances during the polycondensation process because of the different volatility of the components. In the course of the work it was established that disturbance of the equimolecular relationship of the initial substances took place because of the volatility of the diamine. As is known, a change in diamine concentration during the reaction process leads to lowering of the molecular weight as a result of acidolysis [4]. With the object of obtaining a polyamide of higher molecular weight the effect was studied of excess diamine (0.5 to 10% above equimolecular) on the molecular weight and melting point of the polyamide formed. It was shown that a 2% excess of diamine in the polycondensation in both the fusion and solvent processes can raise the molecular weight of the polyamide from 8,500–8,780 to 11,130–12,000, and the melting point from 46 to 78°.



Differential and integral molecular weight distribution curves. 1) Differential curve, 2) integral curve.

It is known that polyamides possess little polydispersity in molecular weight because of intensive interchange processes between the molecules of the polymers, monomers and low-molecular reaction products. This fact was demonstrated by V. V. Korshak and V. A. Zamiatina [5] by the fractionation method and by S. E. Bresler et al. [6] by the method of sedimentation in the ultracentrifuge. Our investigation of the molecular weight distribution of the polyamide indicated a high degree of monodispersity for poly-3,3'-dimethyldiphenylmethaneadipo-N,N'-diethylamide. About 50% of the polymer has molecular weights within the narrow range of 6,000 to 7,000. Integral and differential molecular weight distribution curves are shown in the diagram.

Examination of the melting-point and molecular-weight data (Table 1) of the polyamide obtained allows the conclusion to be drawn that there is a linear relationship between them.

The equation which expresses this relationship analytically was derived graphically; this equation has the following form:

$$T_{\text{m.p.}} = \frac{M - 4000}{96.2},$$

where M is the molecular weight of the polyamide.

TABLE 1

Molecular weight, determined viscometrically	8500	8780	10370	11130	10550	8780	8500
Melting point	46°	52°	65°	78°	65°	52°	47°

In order to verify the relationship found, a number of samples of poly-3,3'-dimethyldiphenylmethaneadipo-N,N'-diethylamide were specially prepared and their melting points and viscometric molecular weights determined. Comparison of these molecular weights with the molecular weight figures calculated from the melting points confirms the correctness of the relationship established (Table 2).

TABLE 2

Melting point	Molecular weight		Relative error (in percent)
	determined viscometrically	calculated from the melting point	
38°	7560	7650	1.2
75	11360	11215	0.9
76	11360	11310	0.1
79	11600	11600	0.0

For the purpose of studying the possibility of obtaining a polyamide of higher molecular weight we set up a series of catalyzed polycondensation experiments. It is known [3] that phosphoric acid acts as a catalyst in the process of polyamide formation. In the present work another side of this question was investigated, namely the effect of phosphoric acid on the molecular weight of the polyamide. It was discovered that addition of 0.3–2.1% of phosphoric acid causes a relative lowering of molecular weight of approximately 4,000–2,000. The addition of 3% or more of phosphoric acid does not affect the molecular weight of the polyamide. At increased temperatures (265-275°) in the presence of phosphoric acid, infusible and insoluble polymers were formed, evidently in consequence of cross-linking between separate polyamide chains.

EXPERIMENTAL

The synthesis of poly-3,3'-dimethyldiphenylmethaneadipo-N,N'-diethylamide was carried out by heating mixtures of N,N'-diethyl-4,4'-diamino-3,3'-dimethyldiphenylmethane and adipic acid in a three-necked flask or in special equipment, on a Wood's metal bath in a current of CO_2. Before determining the molecular weight the polymer was broken up and freed from monomer residues by heating in a 10% aqueous methanol solution.

For determining the magnitude of K_m of methanol solutions of the polyamide under investigation, the method of chemical determination of end groups was used. For this purpose polyamides of low degrees of polycondensation were specially prepared and the acid and amine numbers of the initial monomer mixture (AN_0 and AmN_0) and of the end product (AN and AmN) were determined. On the basis of the experimental results the degree of conversion of monomers to polymer (p), the degree of polycondensation (n) and the molecular weight (M) were calculated. The following relationships were used in the calculations:

$$p = \frac{AmN_0 - AmN}{AmN_0};\quad p = \frac{AN_0 - AN}{AN_0};\quad n = \frac{1}{1-p};\quad M = M_0 + 18,$$

where M_0 is the molecular weight of the elementary chain segment. The results are given in Table 3.

TABLE 3

Weight of sample (in g)	AN_0	AN	AmN_0	AmN	p	n	M_0	M
1.3370	262	20	–	–	0.923	13	392	5114
1.5961	–	—	170	12	0.928	14	392	5506

For the calculation of K_m, which was found to be $10.75 \cdot 10^{-4}$, the mean of two molecular weight determinations and the specific viscosity of a 0.5% solution of the polyamide in methanol ($\eta_{spec.}$ 0.058) were used.

With the object of determining the optimum reaction conditions the polycondensation was carried out at 220 and 250–255°. During the course of the reaction, test samples of the reaction mixture were removed for determination of their acid and amine numbers and molecular weights. These experiments showed that the reaction proceeded to the greatest extent in the first hour. There is no advantage in heating for more than 5 hours because in the first 2–3 hours the molecular weight rises to 3,000–5,000 (depending on the reaction temperature) and the acid number falls from 262 to 35.0; during the next 2 hours the molecular weight rises only to 5,000–5,500. When vacuum treatment is included a new, sharp rise in molecular weight to approximately 7,000–9,000 is observed. Increasing the reaction time in vacuo beyond 2 hours is also of no advantage since the increase in molecular weight again ceases.

In the study of the effect of reaction temperature on the properties of the polyamide (molecular weight, acid and amine number) experiments at 140 and 260° were carried out under the conditions described above. The results are given in Table 4.

TABLE 4

Properties of polyamide	Reaction temperature							Initial values
	140°	160°	180°	200°	220°	240°	260°	
Molecular weight determined viscometrically (K_m $10.45 \cdot 10^{-4}$). . . .	1790	3110	5000	6200	8470	9050	9330	–
Amine number	62.1	49.2	44.5	39.5	24.8	20.2	16.2	170
Acid number	74.2	69.3	64.5	60.0	45.0	31.7	27.0	262

For the study of polydispersity a weighed sample of the polyamide (50.2 g) was dissolved in 1200 ml of methyl alcohol; fractionation was carried out by the method of fractional precipitation of the polyamide with

distilled water from a 0.5% solution of the polymer. The weight and molecular weight (viscometric) of each sample separated was determined after drying in a vacuum desiccator. Integral and differential molecular weight distribution curves were constructed from the results obtained.

SUMMARY

1. Poly-3,3'-dimethyldiphenylmethaneadipo-N,N'-diethylamide, which is soluble in ordinary organic solvents, has been synthesized for the first time. The effect of N-substitution on the properties of the polymer has been determined. The optimum conditions of preparation have been found.

2. The value of K_m for alcoholic solutions of the polyamide was found to be $10.75 \cdot 10^{-4}$.

3. Differential and integral molecular-weight distribution curves of the polyamide have been constructed, a low degree of polydispersity being found.

4. An equation has been derived connecting the melting point of poly-3,3'-dimethyldiphenylmethane-adipo-N,N'-diethylamide with its molecular weight.

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THE SYNTHESIS OF N-SUBSTITUTED METHACRYLAMIDES

IV. ACYLATION OF AROMATIC AMINES WITH METHACRYLYL CHLORIDE IN AN AQUEOUS MEDIUM

T. A. Sokolova and L. A. Ovsiannikova

The difference observed between the hydrolysis rate of methacrylyl chloride and its reaction rate with aromatic amines made it possible for us to conduct the acylation of amines in an aqueous medium. Previously, N-arylmethacrylamides were prepared in an organic solvent medium [1,2].

As the experiments showed, N-arylmethacrylamides may be prepared in good yields by adding 1 mole of methacrylyl chloride to an emulsion or a suspension of 2 moles of aromatic amine in water with vigorous stirring. In this case the water served as a diluent. The second mole of amine combined with the hydrogen chloride molecule evolved during the reaction and passed into the aqueous solution in the form of the hydrochloride. The N-arylmethacrylamide separated either as a liquid layer or in the solid state and could be isolated by filtration or extraction. The reaction products obtained were only slightly colored and had definite melting points. The dried products were further purified by recrystallization or distillation under reduced pressure.

N-Arylmethacrylamides

Name of monomer	Yield of crude product (in %)	Melting point	
		crude product	pure product
m-Fluorophenylmethacrylamide	87.5	71.5–72°	73–73.5°
p-Fluorophenylmethacrylamide	69	70.5–71	73–73.5
p-Iodophenylmethacrylamide	75	135–135.5	137.5–138
m-Methoxyphenylmethacrylamide	92	79–81	92.5–93
p-Dimethylaminophenylmethacrylamide	90	129.5–131	131–131.5
o-Methoxyphenylmethacrylamide	89.8	liquid	b.p. 141° at 2 mm
o-Ethoxyphenylmethacrylamide	89.0	40–40.5	44.5–45
m-Ethoxyphenylmethacrylamide	68	94–95	95.5–96
Phenylmethacrylamide	84.5	83.5–84.5	85–85.5
o-Tolylmethacrylamide	72.8	92.5–93	94.5–95
m-Chlorophenylmethacrylamide	82.4	103.5–104.5	105–105.5
p-Chlorophenylmethacrylamide	80.5	110.5–111.5	112–112.5
p-Methoxyphenylmethacrylamide	77.5	88–89	90.5–91
p-Tolylmethacrylamide	84.5	85–86	88.5–89

The experimental results on the preparation of N-arylmethacrylamides in an aqueous medium are given in the table. The melting point of the reaction products are corrected.

The acylation may also be carried out by substituting 1 mole of the starting amine by 1 mole of dimethylaniline, which does not react with methacrylyl chloride and is a substance which combines with hydrogen chloride. The product yields did not decrease as a result of this substitution.

The yield of N-arylmethacrylamide was almost half the amount when equimolecular amounts of the reagents were used. 1 mole of amine per mole of methacrylyl chloride was sufficient only in the preparation of p-dimethylaminophenylmethacrylamide, as the starting p-dimethylphenylenediamine was itself capable of combining with the hydrogen chloride through its dimethylamino group.

In the case of acylation of solid amines which were insoluble in water, it was advantageous to grind them well first. Using this method we were able to obtain a good yield of o-ethoxyphenylmethacrylamide which was prepared in the form of a polymer when the reaction was carried out in an organic solvent medium [2]. Previously, this monomer has been obtained only via an organomagnesium compound [3].

The method developed however, cannot be applied to the preparation of N-arylmethacrylamides from amines of such low basicity as diphenylamines ($K^{25}_{bas.}$ $7.60 \cdot 10^{-14}$) [4], apparently due to the low rate of acylation of this amine with methacrylyl chloride.

EXPERIMENTAL•

Preparation of N-arylmethacrylamides. 0.4 mole of the aromatic amine was stirred with 100 ml of water in a two-necked, round-bottomed flask, fitted with a stirrer and a dropping funnel. With very vigorous stirring, 0.2 mole of methacrylyl chloride was added dropwise over a period of about 2 hours to the emulsion or suspension of the amine in water. At the end of the addition the mass was acidified with hydrochloric acid until Congo paper gave a blue color and stirred for another half hour, and then the solid N-substituted methacrylamide produced was filtered off, washed with water until neutral and dried at 45–60°. If the reaction product was a liquid, the oily layer which separated was extracted with ether. The extract was dried with anhydrous magnesium sulfate, the ether distilled off and the residue distilled under reduced pressure. The crude product was purified either by recrystallization or redistillation in vacuum.

Preparation of N-p-dimethylaminophenylmethacrylamide. After adding the methacrylyl chloride, we obtained a solution, from which the product was isolated by the addition of alkali until paper soaked in brilliant yellow gave a pale red color. The precipitate of p-dimethylaminophenylmethacrylamide formed was filtered off and then treated as described above.

Properties of new N-arylmethacrylamides

m-Fluorophenylmethacrylamide formed white crystals, which were soluble in acetone, benzene, alcohol, methyl methacrylate and chloroform in the cold and insoluble in water.

Found %: N 7.90; F 10.64. $C_{10}H_{10}ONF$. Calculated %: N 7.71; F 10.61.

p-Fluorophenylmethacrylamide was a white crystalline substance, soluble in acetone, benzene, methyl methacrylate and chloroform in the cold and insoluble in water.

Found %: F 10.53. $C_{10}H_{10}ONF$. Calculated %: F 10.61.

p-Iodophenylmethacrylamide formed fine, white crystals which were soluble in acetone, benzene, alcohol and chloroform and insoluble in water.

Found %: C 41.83; H 3.52; N 4.83; I 44.45. $C_{10}H_{10}ONI$. Calculated %: C 41.81; H 3.49; N 4.87; I 44.25.

m-Methoxyphenylmethacrylamide gave white crystals, which were soluble in acetone, alcohol, benzene and chloroform in the cold and insoluble in water.

Found %: C 69.36; H 6.96; N 7.74. $C_{11}H_{13}O_2N$. Calculated %: C 69.11; H 6.81; N 7.33.

p-Dimethylaminophenylmethacrylamide crystallized from alcohol as yellow prisms. They were soluble in acetone, chloroform and methyl methacrylate in the cold; dissolved in alcohol and benzene on heating and were insoluble in water.

• With the assistance of A. M. Kashnitskaia.

Found %: C 70.55; H 7.98; N 13.78. $C_{12}H_{16}ON_2$. Calculated %: C 70.59; H 7.84; N 13.72.

SUMMARY

1. A method was developed for preparing N-arylmethacrylamides in an aqueous medium, which makes it possible to obtain even readily polymerizable monomers (such as o-ethoxyphenylmethacrylamide). The method was tested by the acylation of 14 aromatic amines with $K_{bas.}$ of the order of 10^{-9}–10^{-11}.

2. Five new N-arylmethacrylamides were obtained: p-iodo-, m-fluoro-, p-fluoro-, m-methoxy- and p-dimethylamino-phenylmethacrylamides.

3. It was shown that the method found was unsuitable for the acylation of amines of low basicity, $K_{bas.}$ of the order of 10^{-14}, (such as diphenylamine) using methacrylyl chloride.

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SULFOLYSIS OF THE SULFONYL GROUPS IN AROMATIC SULFONIC ACIDS

F. M. Vainshtein and E. A. Shilov

A study of the migration of sulfonyl groups showed that these reactions proceed preferentially by the hydrolysis of sulfonic acids followed by the sulfonation of the aromatic compound formed [1]. However, cases are known where the sulfonyl groups were transferred in anhydrous sulfuric acid and even in oleum, i.e. under conditions which exclude hydrolysis [2,3]. Some authors considered this fact as proof of the intramolecular mechanism of the migration of sulfonyl groups in aromatic sulfonic acids [3]. But such a conclusion is difficult to accept on stereo-chemical grounds: for example, it is improbable that the sulfonyl groups of 1,5-naphthalenedisulfonic acid could actually move to positions 2 and 7 without their bond with the aromatic nucleus being broken for a moment. At the same time there would be no need to postulate the intramolecular mode of sulfonyl group migration in the absence of water, if we consider that the acceptor role of an SO_3 molecule may be taken over by other anionoids. In particular, sulfuric acid and its anion may combine with SO_3 to form pyrosulfuric acid and the anion $HS_2O_7^-$. Thus, the sulfonyl group migration could occur intermolecularly, not through hydrolysis but by passing through the stage of sulfolysis.

We decided to check this hypothesis, using sulfur S^{35} as a radioactive indicator. The investigations required sulfonic acids which were incapable of further sulfonation, as the introduction of radioactive sulfonyl groups into the unsubstituted positions in the molecule would have made the analysis of the exchange reactions more difficult. We chose, 2,4,6-toluenetrisulfonic acid (TTS) and 2,4,6-phenoltrisulfonic acid (PTS) for our experiments. The method consisted of heating each of these trisulfonic acids with radioactive fuming sulfuric acid or, on the contrary, the radioactive sulfonic acid was heated with nonradioactive oleum. Then the trisulfonic acid or H_2SO_4 was isolated from the reaction products, purified and its radioactivity determined.

EXPERIMENTAL

Preparations. 2,4,6-Toluenetrisulfonic acid was prepared by successive sulfonations of toluene by Claisen's method [4]. Toluenedisulfonic acid was obtained first and this was converted to its potassium salt and heated to 240° with HSO_3Cl. The excess sulfuric acid was removed with barium carbonate and the filtrate treated with potassium sulfate. After separation of the $BaSO_4$ precipitate, the filtrate contained the potassium salt of TTS with traces of the disulfonic acid. To prepare pure TTS, 1 mole of the potassium salt, dried at 130–140°, was mixed with 3 moles of PCl_5 and the mixture kept at 120–130° for 1 hour and then at 150° for half an hour. The excess PCl_5 was decomposed with cold water and the solid toluenetrisulfonyl chloride filtered onto a glass filter and treated with ether, which dissolved the toluenedisulfonyl chloride. The residue was recrystallized from chloroform until the melting point was 153°. The toluenetrisulfonyl chloride obtained was hydrolyzed by boiling under reflux with 14 parts of water. The filtered solution was evaporated on a water bath until the HCl had been removed completely. The yellow sirup obtained deposited white crystals of 2,4,6-toluenetrisulfonic acid after cooling. After being dried in vacuum over sodium hydroxide, the crystals contained 6 molecules of water per molecule of TTS according to analysis, which agreed with Claisen's data [4].

To prepare 2,4,6-phenoltrisulfonic acid, we heated phenol with chlorosulfonic acid for 5 hours at 130–140° [5]. The precipitate of phenoltrisulfonyl chloride formed was recrystallized twice from $CHCl_3$; the m.p. was 192°. The 2,4,6-phenoltrisulfonyl chloride was immediately hydrolyzed in water. After evaporation and cooling, the solution deposited crystals of PTS. The preparation was dried in vacuum and had the composition $C_6H_6O_{10}S_3 \cdot 3\frac{1}{2} H_2O$.

To prepare radioactive oleum or chlorosulfonic acid, we dissolved dry $Na_2S^{35}O_4$ in them.

The radioactivity was determined using such thin layers of the barium salts of the sulfonic acids that the self-absorption of the β-rays by the samples could be ignored. For these conditions, the thickness of the layers of TTS and PTS barium salts had to be not more than 6.5 mg/cm^2, and not more than 8 mg/cm^2 for $BaSO_4$. The precipitates were deposited on tared aluminum discs from fine suspensions in methanol. The weight was determined by difference after drying the sample at 100°. The emitting surface was 0.63 cm^2. The radioactivity was measured using an end-window tube housed in a lead castle and connected to a B type counting unit. Each radioactivity determination was repeated several times. We estimated the probable error in the average values at ±3%.

We performed the experiments on the sulfolysis of sulfonic acids in sealed glass ampules, into which were placed from 0.07 to 0.1 g of TTS or PTS and sufficient radioactive or nonradioactive oleum (0.1–0.4 g) so that there remained excess SO_3 after the water of crystallization had been bound as H_2SO_4. The free SO_3 content was determined by analysis in control experiments. The ampules were heated for a known time in an aluminum block, the contents dissolved in water and the sulfuric acid precipitated with an aqueous suspension of $BaCO_3$. The filtrate was evaporated to dryness; samples were taken from the residue for activity determination. The percentage of exchange was calculated from the ratio of the observed radioactivity of the barium salt (R) to the calculated value for its activity at complete exchange (R_0).

Sulfolysis of 2,4,6-toluenetrisulfonic acid

A. Nonradioactive TTS was treated with radioactive oleum. The results of two experiments at 212° in this series are illustrated in Fig. 1. In the experiment illustrated by Curve 1, the free SO_3 content of the mixture was 8.5% and R_0 = 87 counts/mg/min. In the experiment illustrated by Curve 2, the free SO_3 content was 23% and R_0 = 300 counts/mg/min. Curves 1 and 2 show that in fuming sulfuric acid the sulfonyl groups of TTS undergo exchange at a measurable rate. The reaction was accelerated by increasing the SO_3 concentration in the fuming sulfuric acid.

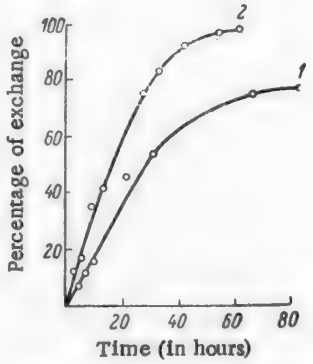


Fig. 1. Exchange of sulfonyl groups between 2,4,6-toluenetrisulfonic acid and radioactive fuming sulfuric acid. 1) 8.5% free SO_3, 2) 23% free SO_3.

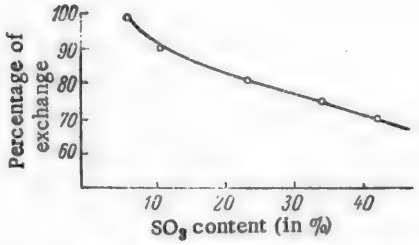
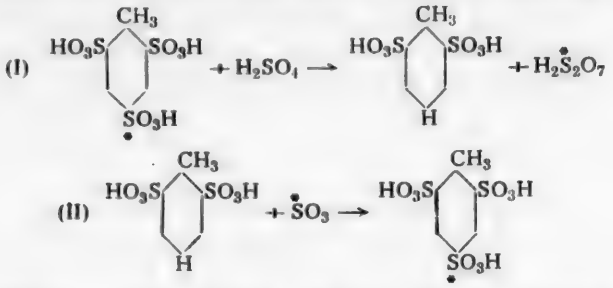


Fig. 2. Exchange of sulfonyl groups between radioactive 2,4,6-toluenetrisulfonic acid and nonradioactive fuming sulfuric acid with various SO_3 contents.

B. On the other hand, if the sulfolysis was performed in nonradioactive fuming sulfuric acid on radioactive TTS, then the percentage of exchange decreased with an increase in the SO_3 content of the mixture. The appropriate data are illustrated in Fig. 2 and are taken from a series of experiments performed at 212°. R_0 = 80–180 counts/mg/min and the heating time was 9 hours.

To explain this difference in the results from two identical exchange processes, one should take into consideration the fact that the reaction products examined in series A and B were not the same. In the first series we determined the radioactivity of the final product of sulfonation in the form of 2,4,6-toluenetrisulfonic

acid and in the second, the radioactivity of the sulfuric acid, which controls the elimination and transfer of the sulfonyl group in the solution. At the same time, according to our postulate, the exchange of sulfonyl groups proceeds in two stages: I—actual sulfolysis of one or two sulfonyl groups, II—sulfonation.



Apparently, the reaction rate is limited by stage II and stage I proceeds relatively quickly. Therefore, if we consider series B, which is illustrated in the scheme, the radioactive sulfur will appear in the sulfuric acid at the rate of the sulfolysis. At the same time, when we determine the radioactivity of the TTS as in series A, we will observe the slower sulfonation of toluenedisulfonic acid. Therefore, increasing the SO_3 content retards stage I as it reduces the concentration of the proton donor—the H_2SO_4 molecule. On the other hand, the rate of stage II is increased by increasing the SO_3 content as together with this we are increasing the concentration of SO_3H^+, which is apparently the most active sulfonating agent [6].

2,4,6-Phenoltrisulfonic acid

The exchange was carried out at 115° with various concentrations of SO_3 in the mixture. The results of experiments with nonradioactive PTS and radioactive oleum are given in the Table and in Fig. 3.

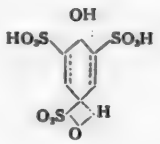
TABLE

Exchange of Sulfonyl Groups (in Percent) Between Nonradioactive 2,4,6-phenoltrisulfonic Acid and Radioactive Sulfuric Acid with Various SO_3 Concentrations.

Medium	Heating time (in hours)					
	1	2	3	4	5	7
94% H_2SO_4 .	17	53	60	70	79	80
100% H_2SO_4 .	22	54	59	66	75	83
11% SO_3 . .	17	50	60	68	—	89
34% SO_3 . .	—	53	61	75	82	86
47% SO_3 . .	16	53	—	69	77	87

The figures given in the Table show that the rate of exchange in PTS does not depend on the concentration of SO_3 in the mixture. This remarkable relationship apparently has to be explained by the fact that rate of SO_3H exchange firstly limits the total reaction rate and secondly, this reaction does not require H_2SO_4 as the SO_3H acceptor.

It is possible that the proton donor is a sulfonyl group of the phenoltrisulfonic acid itself and the exchange proceeds through an intermediate complex.



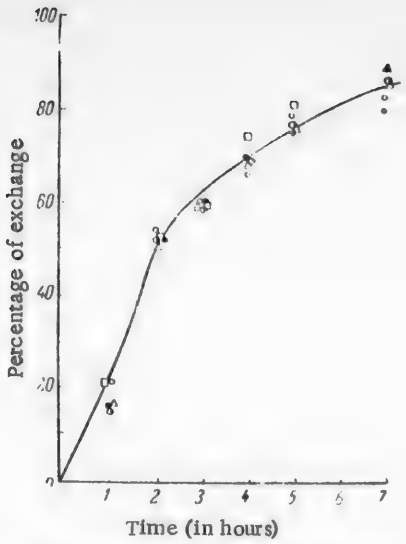


Fig. 3. Exchange of sulfonyl groups between nonradioactive 2,4,6-phenoltrisulfonic acid and radioactive sulfuric acid with various SO_3 concentrations.

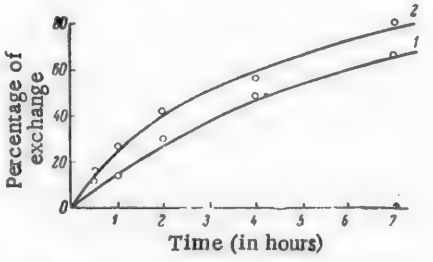


Fig. 4. Exchange of sulfonyl groups between radioactive 2,4,6-toluenetrisulfonic acid and nonradioactive sulfuric acid. 1) Without additions, 2) with 20% K_2SO_4 added.

Fuming sulfuric acid is only an inert solvent in the first stage and the stage of PTS sulfonation proceeds relatively rapidly and does not affect the total exchange rate.

Exchange experiments with 2,4,6-toluenetrisulfonic acid in aqueous sulfuric acid

Several experiments with TTS were performed under conditions where hydrolysis of sulfonyl groups was possible, namely, in 91% sulfuric acid. In this case we used radioactive TTS and nonradioactive sulfuric acid and therefore observed the rate of stage I (Fig. 4). Because of the increase in reaction rate, the reaction temperature could be lowered to 175°. Nevertheless, heating was accompanied by tar formation and oxidation, which appeared as darkening and the evolution of SO_3. At the same time, these effects were hardly noticeable during heating in oleum.

Some experiments were carried out with K_2SO_4 added as an acceptor for HO_3S groups. As Fig. 4 shows, large additions of sulfate (20%) accelerate the reaction noticeably, confirming the acceptor action of K_2SO_4. The addition of 3% of this material did not produce a noticeable effect. This is readily understood as potassium sulfate competes with water as a proton acceptor.

We should also like to mention the fact that using the information on the catalytic effect of anhydrous ferric chloride on the rearrangement of 1,5-naphthalenedisulfonic acid [2], we performed experiments on the exchange of sulfonyl groups by radioactive PTS in the presence of $FeCl_3$, but the addition of this material had no effect.

SUMMARY

1. The exchange of sulfonyl groups of 2,4,6-toluenetrisulfonic acid (TTS) at 212° and 2,4,6-phenoltrisulfonic acid (PTS) at 115° with fuming sulfuric acid, containing various amounts of SO_3, was studied. S^{35} was used as a radioactive indicator.

2. It was shown that the exchange of sulfonyl groups in TTS proceeded in two stages: I - the substitution of the HO_3S group by H (sulfolysis) and II - the sulfonation of the sulfolysis product to TTS. Stage I was retarded and stage II accelerated by an increase in the SO_3 content of the sulfuric acid.

3. The rate of the HO_3S group exchange in PTS did not depend on the SO_3 concentration in the sulfuric acid.

4. It was postulated that the mechanism of TTS sulfolysis involved the participation of SO_3 acceptors in the form of sulfuric acid, which is converted to pyrosulfuric acid. It is possible that in PTS sulfolysis a sulfonyl group of the PTS molecule itself was the proton donor.

5. The exchange of sulfonyl groups of TTS with 91% aqueous sulfuric acid was accelerated by adding K_2SO_4.

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CATALYTIC REDUCTION OF BENZALDEHYDE

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As is known, aldehydes and ketones may be converted into hydrocarbons by reduction with hydrogen iodide and phosphorus [1,2, 4–8] or through appropriate hydrazones by Kizhner's method [3]. In the last few years, a number of papers have been published on the reduction of furfural to sylvan [9–15] and benzaldehyde to toluene [16–22]. Recently Sultanov and Maslennikova [23] proposed a new copper-zinc-aluminum alloy catalyst, similar to Devarda's alloy, for the reduction of furfural to sylvan.

In this work we studied the reduction of benzaldehyde over this copper-zinc-aluminum catalyst. The results are given in Table 1.

TABLE 1

Experiment no.	Temperature	Content of products in catalyzate (in %)			Losses (in %)
		toluene	benzyl alcohol	benzaldehyde	
1	100°	—	—	100	—
2	150	19.0	53	16.6	11.4
3	175	26.2	54	6.6	13.2
4	200	63.5	11.4	6.6	18.5
5	225	87.0	1.6	—	11.4
6	300	87.4	2.4	–	10.2

The data in Table 1 show that the best results in the reduction of benzaldehyde to toluene over the copper-zinc-aluminum catalyst were obtained in the temperature range of 200–300°. The considerable losses apparently were mainly because of the process being intermittent, for when it was carried out continuously at 250° the losses were reduced to 5% with a toluene yield of 91% and a 4% yield of benzyl alcohol.

The reaction mechanism of benzaldehyde reduction to toluene using various catalysts has hardly been studied. According to the data given by Ipatiev, benzaldehyde is reduced on an iron surface through the intermediate stage of benzyl alcohol formation [18]. Such a mechanism is also possible on precipitated copper catalysts, supported on dehydrogenating substances such as clay, oxides of aluminum, chromium and thorium, silicon dioxide etc. As carbonyl compounds are reduced on these catalysts at relatively high temperatures, the hydroxyl groups of the intermediate alcohols may be substituted by hydrogen atoms. As benzaldehyde was reduced on our catalyst at quite a low temperature (from 150 to 300°) and the catalyst contained metallic zinc, this reaction on the copper-zinc-aluminum catalyst may be compared with Clemmensen's reaction.

It is interesting to note that the reduction of benzaldehyde to toluene by Clemmensen's method gave a considerable yield of the latter. However, under the same conditions benzyl alcohol gave not more than 6% of toluene, as our tests showed. Also a small amount of benzyl chloride and a great deal of an undistillable liquid with a sharp smell, were isolated from the residue. These data contradict the carbinol mechanism of benzal-

dehyde reduction by Clemmensen's reaction and raise doubts on the carbinol mechanism of benzaldehyde reduction to toluene on a copper-zinc-aluminum catalyst as well. Characteristically, furfural gave up to 85% of sylvan on a copper-zinc-aluminum catalyst at 225-250° while under the same conditions furfuryl alcohol gave only a 45% yield of sylvan.

These data seem to indicate that the reduction of the aldehyde group to the methyl group does not proceed through a stage of alcohol formation, but directly. In order to confirm this hypothesis we passed benzyl alcohol through the catalyst without introducing hydrogen from outside. This gave benzaldehyde (see Table 2) in decreasing yield with increased temperature, and toluene in increasing yield with increased temperature. On this basis, one may consider that the reaction begins with dehydrogenation of the benzyl alcohol. The fall in benzaldehyde yield with increasing temperature and the rise in toluene yield are apparently a result of the more intense reduction of benzaldehyde to toluene than to alcohol and not inhibition of the reaction by dehydrogenation of the alcohol.

TABLE 2

Experiment no.	Temperature	Content of products in catalyzate (in %)			Losses (in %)
		benzaldehyde	toluene	benzyl alcohol	
1	150°	68.0	16.9	11	4.1
2	200	59.6	27.4	10	3.0
3	250	57.9	32.4	6.6	3.1
4	300	39.0	58.5	0.0	2.5

On the other hand, the data obtained show that the temperatures 250–300°, at which benzaldehyde is successfully reduced, are most unsuitable for the existence and therefore, the formation of benzyl alcohol from benzaldehyde. In the fourth experiment in Table 2, the toluene yield does not correspond to the consumption of hydrogen evolved during dehydrogenation of the benzyl alcohol. This may be explained by the participation of hydrogen, chemosorbed on the catalyst surface.

A smaller amount of furfuryl alcohol was converted to furfural and sylvan at 225–250° than benzyl alcohol to benzaldehyde and toluene: only 19.3% of furfural and 12% of sylvan were formed.

Benzyl alcohol was successfully converted to toluene on the copper-zinc-aluminum catalyst when it was passed through with hydrogen (Table 3) which was apparently due to the ease with which this alcohol is dehydrogenated.

TABLE 3

Experiment no.	Temperature	Content of products in catalyzate (in %)			Losses (in %)
		toluene	benzyl alcohol	benzaldehyde	
1	150°	52.5	46	0	1.5
2	200	75.6	23	0	1.4
3	250	90	5.9	0	4.1

The absence of traces of benzaldehyde during benzyl alcohol reduction (Table 3) may also be explained by the fast conversion of benzaldehyde to toluene. Therefore, the benzyl alcohol residue in experiments 2 and 3 (Table 3) are greater than the alcohol yields in experiments 4–6 (Table 1), in spite of the large excess of hydrogen used in the experiments in Table 3. Finally, it is interesting to note that ethyl alcohol was not dehydrogenated to acetaldehyde in the range 200–350° on the copper-zinc-aluminum catalyst and that no notice-

able reduction to ethane occurred in a current of hydrogen; in connection with the acetaldehyde, at 200–350° it was completely hydrogenated in a current of hydrogen to ethyl alcohol. No ethane formation was observed in this experiment.

These data indicate that benzaldehyde reduction to toluene on a copper-zinc-aluminum catalyst proceeds directly, while benzyl alcohol is converted to toluene mainly through benzaldehyde. The same may be said of furfural and furfuryl alcohol under the same conditions.

EXPERIMENTAL

A reactor consisting of a stainless steel tube, 40 mm in diameter and 650 mm high, was placed in a vertical furnace with a temperature control device. A 400 mm layer of catalyst was placed exactly in the center of the reactor. This required 500 ml of granulated catalyst weighing 800 g and with a particle diameter of 3–4 mm. A thermocouple housing was passed through the lid into the center of the reactor. Materials were fed into the reactor from a burette at the top, under slight pressure. The catalyzate (together with excess hydrogen) was led through a normal cooling system, cooled with ice then with solid carbon dioxide. The starting material was fed in at a rate of 60 ml/hour with a 5 molar amount of hydrogen.

The preparation method, quantitative composition and activation method for the catalyst were described previously [23].

Reduction of benzaldehyde (Table 1, experiment 4). 60 ml of benzaldehyde (62.76 g) was steadily fed into the reactor from the burette over a period of 1 hour with the catalyst bed at 200°. At the same time, hydrogen was fed in at a rate of 66.5 liters/hour, while the excess escaped into the atmosphere. The catalyzate passed from the reactor, through a water condenser and into a receiver, cooled with an ice mixture. For the condensation of possible volatile products, another receiver was attached and this was cooled with solid carbon dioxide. After removal of the aqueous layer, the whole catalyzate was treated with sodium bisulfite solution to remove benzaldehyde. Toluene and benzyl alcohol were separated by a normal distillation. We obtained 4.2 g (6.6%) of benzaldehyde, 34.6 g (63.5%) of toluene with b.p. 108–110°, $n^{20}D$ 1.4952 and 7.3 g (11.4%) of benzyl alcohol with b.p. 200°, $n^{20}D$ 1.5396 (benzyl bromide was prepared).

Reduction of furfural. 100 ml of furfural was fed into the reactor steadily over a period of 3 hours 20 minutes at 225–250°. During this period 230 liters of hydrogen was passed in. The aqueous layer was separated from the combined catalysts from the two receivers and the catalyzate dried over anhydrous sodium sulfate. Distillation of the dried catalyzate from a normal flask with a pear fractionating column gave 92 ml of sylvan (85% of the furfural used) with b.p. 60–65°, $n^{20}D$ 1.4340 and 6 ml (12%) of furfuryl alcohol with b.p. 165–172°, $n^{20}D$ 1.4860.

Reduction of furfuryl alcohol. 30 ml (33.9 g) of pure furfuryl alcohol was passed through the reactor over a period of 60 minutes at 225–250° simultaneously with 60 liters of hydrogen. The aqueous layer was separated from the total catalyzate (31 ml), which was then dried over anhydrous sodium sulfate. We isolated 14.5 ml or 13.3 g of sylvan (45% of the starting alcohol) and 15 ml of a high-boiling fraction, from which 1.5 ml (1.7 g) of furfural was isolated by the bisulfite method. The residue contained 14.6 ml (16.5 g) of furfural alcohol (48.7%) with b.p. 166–172°, $n^{20}D$ 1.4860.

Conversion of furfuryl alcohol on the catalyst. 24 ml (27 g) of furfuryl alcohol was fed in over a period of 60 minutes at 225–250° without a stream of hydrogen. We isolated 4.4 ml (5 g) of furfural (19.2%) from the dried catalyst by the bisulfite method and the residue yielded 3 ml (12.1%) of sylvan and 14 ml (15.7 g) of furfuryl alcohol (58%).

Conversion of benzyl alcohol on the catalyst (Table 2, experiment 3). 60 ml (62.6 g) of benzyl alcohol was passed through the catalyst bed at 250° over a period of 1 hour without hydrogen. The dried catalyst yielded 17.3 g of toluene (32.4%), 35.5 g of benzaldehyde (57.9%) and 41.7 g of benzyl alcohol (6.6%).

Reduction of benzyl alcohol (Table 3, experiment 2). 60 ml (62.6 g) of benzyl alcohol and 66.5 liters of hydrogen were passed through the catalyst bed at 200° over a period of 1 hour. From the catalyzate we isolated 39 g of toluene (75.6%) and 14.6 g of benzyl alcohol (23%).

Conversion of ethyl alcohol on the catalyst in a stream of hydrogen. 30 ml of ethyl alcohol and 60 liters of hydrogen were passed through the catalyst at 250 and 300° over a period of 1 hour. The catalyzate was unchanged alcohol. Analysis of the gases for hydrocarbons gave a negative result.

Conversion of ethyl alcohol on the catalyst without the addition of hydrogen. With the catalyst at 250 and at 300°, 30 ml of ethyl alcohol yielded 27 ml of liquid, which was identified as ethyl alcohol. A qualitative reaction for aldehyde was negative.

Conversion of actaldehyde on the catalyst in a stream of hydrogen. 30 ml of acetaldehyde and 60 liters of hydrogen were fed in over a period of 1 hour at 225°. We obtained 24.1 ml of catalyzate, which was dried; this yielded 23.8 g (93.5%) of ethyl alcohol, boiling at 78–80°, with $n^{20}D$ 1.3618. Analysis for hydrocarbons was negative.

Reduction of benzyl alcohol under the conditions of the Clemmensen reaction. 200 g of amalgamated zinc and 150 ml of hydrochloric acid were placed in a liter flask, fitted with a reflux condenser. When the vigorous evolution of hydrogen began, benzyl alcohol (50 g) was introduced dropwise into the sphere of the reaction over a period of 1 hour, then the mixture was boiled for 2 hours with the portionwise addition of a further 50 ml of concentrated hydrochloric acid during this time; the contents of the flask were then diluted with 200 ml of water and the upper, oily layer separated, dried over sodium sulfate and distilled. We isolated 3 ml (6%) of toluene with b.p. 110° and 12 ml of benzyl chloride (24%) with b.p. 178–179°. The residue was an undistillable liquid with a sharp smell and we did not examine it further.

SUMMARY

1. The possibility of using a copper-zinc-aluminum alloy catalyst for reducing benzaldehyde and benzyl alcohol to toluene in a flow system under ordinary pressure was demonstrated.

2. In the absence of hydrogen, benzyl and furfuryl alcohols were dehydrogenated to the corresponding aldehydes, forming simultaneously toluene and sylvan with the hydrogen evolved during the reaction.

3. Benzaldehyde was reduced on a copper-zinc-aluminum catalyst directly without the intermediate formation of benzyl alcohol. The alcohol then formed was the product of a parallel hydrogenation process which occurred mainly at temperatures below the optimal temperatures for the reduction. Under these conditions the alcohols, capable of being dehydrogenated to aldehydes, may be converted to hydrocarbons.

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INVESTIGATION OF OXIDO COMPOUNDS

X. REACTION OF α-OXIDES OF ALLYL ETHERS OF PHENOL, o- AND p-CRESOLS AND GUAIACOL WITH AMINES

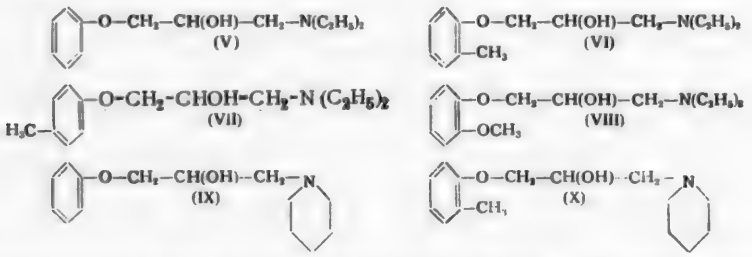
Z. B. Idel'chik and V. I. Pansevich-Koliada

As is known, some derivatives of α-oxides of phenyl allyl ethers are physiologically active preparations [1,2]. Some derivatives of α-oxides of nitrophenyl allyl ethers also possess this property [3].

In order to increase the information available on such compounds, in the present work we reacted α-oxides of the allyl ethers of phenol, o- and p-cresols and guaiacol with diethylamine and α-oxides of the allyl ethers of phenol and o-cresol with piperidine.

Oxidation of the allyl ethers of appropriate phenols with acetyl hydroperoxide [4,5] and reaction of the phenols with epichlorohydrin [1,2,6–9] gave the following α-oxides of phenyl allyl ethers: 1-phenoxy-2,3-oxidopropane (I), 1-(o-tolyloxy)-2,3-oxidopropane (II), 1-(p-tolyloxy)-2,3-oxidopropane (III) and 1-(o-methoxyphenoxy)-2,3-oxidopropane (IV).

Gentle heating of the ether oxides obtained (I, II, III, IV) with diethylamine [1,2,6,7,10], and the ether oxides (I and II) with piperidine gave the corresponding phenoxyamino alcohols. On the basis of certain papers [1,2] on the reaction of glycide ethers of phenol with amines, the structures of the phenoxyamino alcohols we obtained may be expressed by the following formulas. (V–X): 1-phenoxy-3-diethylamino-propanol-2 (V), 1-(o-tolyloxy)-3-diethylaminopropanol-2 (VI), 1-(p-tolyloxy)-3-diethylaminopropanol-2 (VII), 1-(o-methoxyphenoxy)-3-diethylaminopropanol-2 (VIII), 1-phenoxy-3-(N-piperidyl)-propanol-2 (IX) and 1-(o-tolyloxy)-3-(N-piperidyl)-propanol-2 (X).



All the phenoxyamino alcohols mentioned above readily formed water-soluble hydrochlorides and ethiodides. Substances (VI, IX and X) were obtained only in the form of derivatives.

Pharmacological testing of the phenoxyamino alcohols (V–X) and their hydrochlorides and ethiodides showed that they have a strong hypotensive effect with relatively low toxicity.* The toxicity increased from free phenoxyamino alcohols to their hydrochlorides and ethiodides, but the hypotensive effect of these preparations increased in the same sequence.

* The tests were carried out by L. A. Iakubovich in the pharmacology department of the Minsk Medical Institute.

EXPERIMENTAL

1. 1-Phenoxy-3-diethylaminopropanol-2 (V). The α-oxide of the allyl ether of phenol (I) was prepared by oxidizing allyl phenyl ether with acetyl hydroperoxide [4,5] and also by reacting phenol with epichlorohydrin [1,2,6–8] and appeared as a mobile liquid with a weak, tobacco-like smell.

B.p. 242.5° (755 mm), 104° (2 mm), $n^{20}D$ 1.5300, d^{20}_4 1.1190, MR_D 41.54; calculated 41.37.

26 g of diethylamine was added to 23 g of (I) and the mixture heated on a water bath at 60–65° for 5 hours. The excess diethylamine was washed out with water and the reaction products extracted with ether, dried with $MgSO_4$ and vacuum distilled. The substance obtained was a thick liquid, which rapidly darkened in air and was insoluble in water and readily soluble in organic solvents.

B.p. 176–178° (17 mm), $n^{20}D$ 1.5090, d^{20}_4 1.0200, MR_D 65.57; calculated 65.74.

Found %: C 70.01; H 9.79. M 226.1. $C_{13}H_{21}O_2N$. Calculated %: C 70.00; H 9.41. M 233.

Ethiodide. 15 g of (V) and 10.5 g of ethyl iodide were heated under reflux on a water bath for 3 hours. The excess ethyl iodide was distilled off by gentle heating in vacuum and then several recrystallizations from an alcohol–ether mixture yielded yellowish crystals, readily soluble in cold water. The m.p. was 119°.

Hydrochloride. 19 g of (V) was dissolved in 50 ml of absolute ether and dry hydrogen chloride passed into the solution until no more crystals were deposited. The hydrochloride was a liquid at room temperature. On cooling with snow, it formed pretty scales, which were readily soluble in cold water and alcohol.

2. 1-(o-Tolyloxy)-3-diethylaminopropanol-2 (VI). The α-oxide of the allyl ether of o-cresol (II) was prepared by reacting o-cresol with chlorohydrin.

B.p. 123–125° (2 mm), $n^{20}D$ 1.5290, d^{20}_4 1.0884, MR_D 46.47; calculated 45.99.

We should note that oxidation of the allyl ether of o-cresol with acetyl hydroperoxide gave an extremely low yield of the α-oxide of this ether [4].

30 g of (II) and 20 g of diethylamine were heated at 65–70° on a water bath for 4 hours. The diethylamine was washed out with water and the reaction product dried and used for the preparation of the ethiodide and the hydrochloride without distillation.

Ethiodide. 20 g of (VI) and 20 g of ethyl iodide were heated on a water bath at 30–35° for half an hour. The whole material crystallized overnight. Recrystallization from an alcohol ether mixture yielded 7.0 g of a substance which was readily soluble in water. The m.p. was 141.5°.

Hydrochloride. 20 g of (VI) was dissolved in 50 ml of absolute ether and dry hydrogen chloride passed in until no more crystals were deposited. We obtained 16.5 g of the hydrochloride, which was readily soluble in cold water and alcohol. The m.p. was 107° (from an alcohol–ether mixture).

3. 1-(p-Tolyloxy)-3-diethylaminopropanol-2 (VII). 5 g of (III), prepared by oxidizing the allyl ether of p-cresol with acetyl hydroperoxide [5] and by reacting p-cresol with epichlorohydrin [1,2,6–8], was treated with 5.5 g of diethylamine (1 : 2.5 moles). After being heated on a water bath at 60–70° for 4 hours, the reaction mixture had a blood red color. The diethylamine was removed under reduced pressure and the residue vacuum distilled. We obtained 5.8 g of substance.

B.p. 139.5° (1.5 mm), $n^{20}D$ 1.5070, d^{20}_4 1.0055, MR_D 70.15; calculated 70.32.

Found %: C 70.48; H 10.00; N 5.66. M 241.3, 233.9. $C_{14}H_{23}O_2N$. Calculated %: C 70.88; H 9.70; N 5.90. M 237.

Ethiodide. 5 g of (VII) was heated with 3.6 g of ethyl iodide on a water bath at 50° for one and a half hours. On cooling the ethiodide crystallized. Two reprecipitations from alcohol with ether yielded 3 g of substance with m.p. 135.5°.

The hydrochloride of 1-(p-tolyloxy)-3-diethylaminopropanol-2 (VII) was obtained as a thick oil. It was readily soluble in cold water and alcohol.

4. 1-(o-Methoxyphenoxy)-3-diethylaminopropanol-2 (VIII). The α-oxide of the allyl ether of guaiacol was prepared by oxidizing the allyl ether of guaiacol with acetyl hydroperoxide [5].

4 g of the oxide was heated with 4 g of diethylamine (1 : 2.5 moles) on a water bath for 3 hours. After evaporation of the diethylamine, the reaction product was vacuum distilled. We obtained 4 g of substance as a thick, slightly pinkish liquid.

B.p. 167° (5.5 mm), n_D^{20} 1.5153, d_4^{20} 1.0631, MR_D 71.51; calculated 71.98.

Found %: C 66.54; H 9.23. M 248.2. $C_{14}H_{23}O_3N$. Calculated %: C 66.40; H 9.09. M 253.

Ethiodide. 2.5 g of (VIII) and 1.54 g of ethyl iodide were heated on a water bath at 60° for 5 hours. After several days, the whole mixture had crystallized. Two recrystallizations from an alcohol – ether mixture yielded 2 g of the ethiodide with m.p. 104°.

5. Hydrochloride of 1-phenoxy-3-(N-piperidyl)-proponal-2 (IX). To 2 g of the oxide of allyl phenyl ether (I), dissolved in 3 g of alcohol, was added 1.3 g of piperidine. The mixture was heated on a water bath for 2.5 hours. The alcohol and the piperidine were distilled off in vacuum. The residue crystallized. After recrystallization from an alcohol – ether mixture, the substance (IX) was again dissolved in a mixture of alcohol and ether and dry hydrogen chloride passed through this solution until no more crystals were deposited. The hydrochloride was recrystallized from a mixture of alcohol and ether. We obtained 3.0 g of a substance with m.p. 126.5°.

6. Hydrochloride of 1-(o-tolyloxy)-3-(N-piperidyl)-propanol-2 (X). To 3 g of the α-oxide of allyl o-cresyl ether (II), dissolved in 3 g of ethyl alcohol, was added 1.5 g of piperidine. The mixture was heated on a water bath for 3 hours. The alcohol and piperidine were distilled off in vacuum. The residue crystallized. It was dissolved in ether and dry hydrogen chloride passed through the cooled solution. The hydrochloride obtained was dissolved in alcohol and precipitated with ether. We obtained 4.5 g of white crystals. The m.p. was 119°.

SUMMARY

Reaction of α-oxides of allyl ethers of o- and p-cresols and guaiacol with diethylamine and α-oxides of allyl ethers of phenol and o-cresol with piperidine gave the following phenoxyamino alcohols: 1-phenoxy-3-diethylaminopropanol-2, 1-(o-tolyloxy)-3-diethylaminopropanol-2, 1-(p-tolyloxy)-3-diethylaminopropanol-2, 1-(o-methoxyphenoxy)-3-diethylaminopropanol-2, 1-phenoxy-3-(N-piperidyl)-propanol-2 and 1-(o-tolyloxy)-3-(N-piperidyl)-propanol-2. Their ethiodides and hydrochlorides were prepared.

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THE NUMBER OF STABLE OXIDES FORMED BY THE METALS OF THE LONG PERIODS OF THE PERIODIC SYSTEM

S.A. Shchukarev

In 1945 I published an article [1] on the thermal stability of the oxides of manganese and iron, which contained the foundations of a number of thermodynamic postulates essential for the development of the study of those series of chemical compounds of stable form which result from the combination of two individual elements, for example, a given metal and oxygen.

The present work represents a further development and generalization of these postulates.

From as far back as the time of D.I. Mendeleev, eight typical oxide forms have been recognized, corresponding to different degrees of oxidation of the element for whose compounds these forms are established. Particular importance is attached in this connection to the limiting forms of the saturated compounds, and also to the question of which elements are capable of showing more than one form of chemical behavior. In this latter respect, as is well known, considerable differences are observed between elements. Thus, for example, sodium has only one form NaX, while manganese has a whole series of competing forms, a list of which resembles in appearance the series of stable isotopes of an element

$$-\ MnX_2\ MnX_3\ MnX_4 - MnX_6\ MnX_7$$

The form MnX is not found, as a result of its instability, and MnX_2 represents the lower limit of the series of compounds whose existence has been experimentally established; the upper limit of the series, corresponding to the group number of seven, is the form MnX_7, the compound MnX_8 being unstable and absent. In addition there is a gap in the series between MnX_2 and MnX_7 corresponding to the disappearance of the unstable form MnX_5. We may regard the upper limiting form MnX_7, corresponding to the number of outer electrons, to be saturated with manganese.

Turning our attention to an examination of some concrete examples of oxide series, we shall select first of all elements forming oxides which are gaseous under ordinary conditions and thus first of all eliminate the complicating influence of such important factors as the energy of condensation and the crystal lattice geometry.

Let us consider the oxides of carbon, nitrogen and oxygen, with analogous formulas:

C, CO, CO_2
N, NO, NO_2, NO_3
O, OO, OO_2

All of these substances have a central atom to which oxygen atoms are attached. The three series of oxides consist of successive states obtained by the addition of first one and then a second oxygen atom; the addition of a third oxygen atom, resulting in a neutral molecule, is observed only in the formation of the extremely unstable, uncharged free radical NO_3.

Table 1 below gives the energies of formation of the above-mentioned oxides from the free atoms.

The data from Table 1 have been used to construct Figure 1, from which it can be seen that the addition of each successive oxygen atom produces a smaller effect than the addition of the preceding atom; the curves fall less and less steeply, as if anticipating the approach of the saturation state, after which the curve should

TABLE 1

Oxide	Energy of formation (in kcal.)	Δ	Oxide	Energy of formation (in kcal.)	Δ	Oxide	Energy of formation (in kcal.)
CO . . .	− 256	126	CO_2 . .	− 382	-	—	—
NO . . .	− 149	72	NO_2 . .	− 221	51	NO_3 . . .	− 272
OO . . .	− 118	24	OO_2 . .	− 142	-	—	—

start to move upwards. The three curves lie in a definite sequence one below the other: the greatest attractive force is evidently that between the oxygen atoms and carbon.

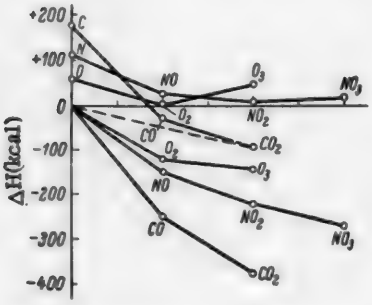


Fig. 1. The energies of formation of oxide molecules for oxygen, nitrogen and carbon from the free atoms (lower group of curves) and from the simple substances (upper group of curves).

If the oxides are prepared not from the free atoms but from the simple substances, energy has first of all to be used up in atomizing the latter. When this factor is taken into consideration, we obtain the values given in Table 2 for the energies of formation of the gaseous molecules from the simple substances.

Since the work of atomization in some cases exceeds the energy of interaction of an oxygen atom with the atoms of the oxidized substance, some of the effects obtained are endothermic.

When the data from Table 2 are added to Figure 1, we obtain three new curves which lie above the previous set.

The starting points of the original curves are raised by 170, 111 and 59 kcal. respectively; the points corresponding to the compounds with formulas RO, RO_2 and RO_3 are raised to different extents:

	RO	RO_2	RO_3
In the case of carbon	170 + 59	170 + 2·59	—
In the case of nitrogen	111 + 59	111 + 2·59	111 + 3·59
In the case of oxygen.	59 + 59	59 + 2·59	—

Thus the farther a point on Figure 1 lies to the right, the higher it is raised in comparison with the points on the same curve which lie to its left. This factor changes the shape of the curves, and, in particular, results in the appearance of minima (for NO_2 and O_2); this is explained by the fact that the vertical distance between the NO_2 and NO_3 points is equal to 51 kcal. on the original curve, i.e., it is less than 59 kcal.; in exactly the same way distance between the O_2 and O_3 points is equal to 24 kcal., i.e., less than 59 kcal. From this it is clear

TABLE 2

Atom	Energy of atomization per g-atom (kcal.)	Oxide	Energy of formation (kcal.)	Oxide	Energy of formation (kcal.)	Oxide	Energy of formation (kcal.)
[C]	+ 170	(CO) . . .	− 27	CO_2. . .	− 94	—	—
(N)	+ 111	(NO) . . .	+ 21	NO_2. . .	+ 8	NO_3. . . .	+ 16
O	+ 59	OO	0	OO_2. . .	+ 35	—	—

that NO_3 and O_3 are capable of liberating part of their oxygen exothermically. It is in this way that the upper limit of stable oxide formation for a particular element may be lowered.

The fairly high energy of atomization of molecular nitrogen and the higher position of the original curve for its oxides compared with the oxides of carbon makes the formation of all the oxides of nitrogen endothermic. In spite of the fact that the energy of atomization of graphite is even higher, the starting position of the CO and CO_2 points is so low that even after they have been raised to the new curves they still lie in the exothermic region; the CO point, however, lies above the broken line connecting the CO_2 point to the origin. Consequently,

CO is capable of exothermic decomposition to carbon and CO_2.

$$\begin{matrix} CO - 40 = [C] + CO_2 \\ +54 \qquad\quad -94 \end{matrix}$$

Thus the lower limit of thermodynamic stability for the oxides of carbon is shifted at low temperatures from CO to CO_2. It is evident that, as in the case of CO, the lower states of oxidation in many other cases may become unstable for elements which have high sublimation energies in the form of the simple substances.

Many other phenomena are dependent on the competition between simple substances and compounds consisting of atoms of different type . Thus, for example, in the formation, from the free atoms, of the oxides and hydrogen compounds of carbon, the quantities of energy liberated are of similar magnitude; in the formation of CH_4 slightly more energy is evolved, even, than in the formation of CO_2 (396 kcal. > 382 kcal.) One has only to consider the formation of the compounds from the simple substances, however, and the picture is altered; CH_4, in fact, becomes a much less stable substance than CO_2. This results from the fact that the atomization of two moles of H_2 requires 208 kcal., while the atomization of one mole of O_2 requires only 118 kcal., i.e., in the first case 90 kcal. more are required. Such molecules as CH, CH_2, CH_3 are all found in the endothermic region and appear as free radicals. These relationships are clearly shown in Figure 2 and in Table 3 [2].

TABLE 3

	Energy of formation (in kcal.)			Energy of formation (in kcal.)	
	from the atoms	from simple substances		from the atoms	from simple substances
C	0	+170			
CH	— 89	+133	$\frac{1}{2}C_2$	— 75	+95
CH_2	—190	+ 84	$\frac{1}{2}C_2H_2$ . . .	—195	+27
CH_3	—286	+ 40	$\frac{1}{2}C_2H_4$ . . .	—270.5	+ 3.5
CH_4	—396	— 18	$\frac{1}{2}C_2H_6$ . . .	—337.5	—11.5
CH_5	—388	+42			

From an examination of Figure 2 we can see that the exothermic phenomena of polymerization of the unsaturated molecules C, CH, CH_2 and CH_3 lead to the formation of dimers, one of which — ethane — now lies in the exothermic region. In addition it should be noted that the question of whether the molecule is odd or even in the sequence evidently has some influence on the energies of formation of the monomeric molecules. Thus, the energies of the successive additions of the second and fourth H atoms, which make the molecules even, are accompanied by a great evolution of energy; as a result, the points lie not on a single curve but on two curves (like the energies of the odd and even isotopes in the series for a given element). It is true that the distance between the curves is small, and after dimerization the phenomenon becomes obscured, since the energies of dimerization decrease regularly from C_2H_2 to C_2H_6.

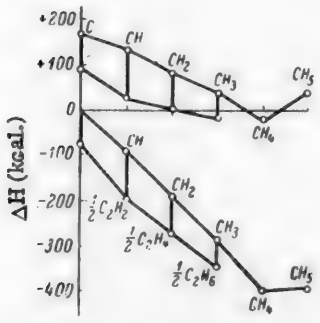


Fig. 2. The energy of formation of hydrocarbons from the free atoms (lower curves) and from the simple substances (upper lines).

In the case of the oxides of hydrogen, as can be seen from Figure 3, the division into odd and even curves is much more clearly defined. At the same time the curves have changed places (as in the case of the isotope series,) the even curve lying not below but above the odd curve, which is related to the fact that hydrogen is the opposite of the even element carbon, i.e., of the artiad element, the hydrogen itself being an odd element (perissad). Figure 3 was constructed using the data [2] given in Table 4.

TABLE 4

	Energy of formation (kcal.)	
	from the atoms	from the simple substances
HO	− 104	+ 7
HO_2	− 169	+ 1
$\frac{1}{2}\ H_2O$	− 111	− 30
$\frac{1}{2}\ H_2O_2$	− 128	− 17

From the examples quoted, we see that gaseous molecules containing an odd number of atoms with even atomic number (i.e., perissad atoms) are less stable and are formed with a smaller evolution of energy. Such molecules strive by some means or other to alter their composition and, in particular, tend to dimerize; this yields molecules containing an even number of electrons.

The effect of the odd or even character of the atoms is even more clearly shown in the case of the oxides of nitrogen and chlorine (Table 5.)

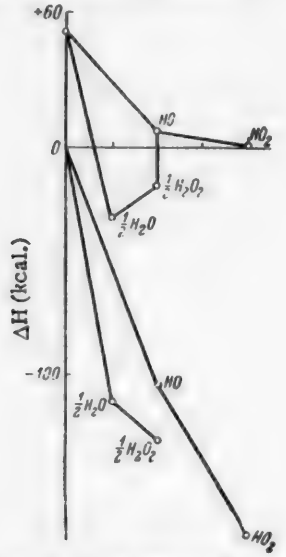


Fig. 3. The energies of formation of the oxides of hydrogen from the free atoms (lower curves) and from the simple substances (upper curves).

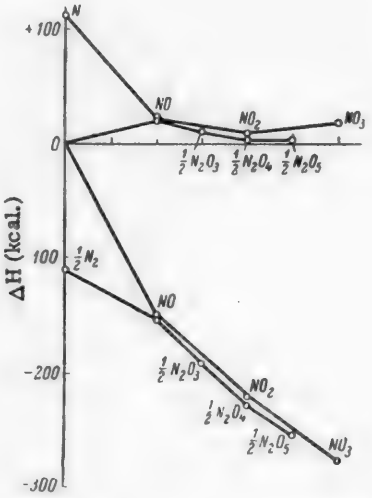


Fig. 4. The energies of formation of the oxides of nitrogen from the free atoms (lower curves) and from the simple substances (upper curves).

All that has been said above relates to gaseous compounds, and there is every reason to suppose that when we change to crystalline substances, and to refractory and nonvolatile substances in particular, we shall encounter a number of peculiar features, as D.I. Mendeleev repeatedly pointed out.

The fundamental state of affairs, in which it is found that the varieties of the saturated forms indicated by the periodic law and depending on the electronic structure of the atom are not always attained in practice, is also found for solid oxides and halides. The classical example of the fact that the limiting stable form found in practice does not always correspond to the theoretical saturation state is provided by the condensed compounds of vanadium; the compositions of the highest compounds given by this element with oxygen and fluorine are V_2O_5 and VF_5, with chlorine VCl_4 and with bromine and iodine VBr_3 and VI_2.

Even in the case of oxides which are normally capable of attaining the normal forms for which the degree of oxidation corresponds to the group number, we have a large number of exceptions. Thus the following solid

and liquid oxides of the elements of Group VIII (iron and its analogs ruthenium and osmium) are known (substances which are metastable in the condensed state are indicated by asterisks:)

–	FeO*	Fe_3O_4	Fe_2O_3	–	–	–
–	–	–	Ru_2O_3*	RuO_2	–	RuO_4*
–	–	–	–	OsO_2	–	OsO_4

Only osmium gives a tetroxide OsO_4 corresponding to the group number and thermodynamically stable even under the conditions of distillation at 100°. The corresponding ruthenium compound RuO_4 decomposes explosively at a temperature of approximately 100°, liberating part of its oxygen and forming RuO_2. The highest thermodynamically stable oxide of iron at low temperatures is Fe_2O_3; the oxides corresponding to higher states of oxidation of iron are all unstable, are not found in the free state, and require for their stabilization the formation of complex compounds, for example, the ferrates.

TABLE 5

	Energy of formation (kcal.)	
	from the atoms	from simple substances
NO	−149	+21
$\frac{1}{2}N_2O_2$	−150.5	+20.5
$\frac{1}{2}N_2O_3$	−189.5	+10
NO_2	−221	+ 8
$\frac{1}{2}N_2O_4$	−227	+ 2
$\frac{1}{2}(N_2O_5)$	−256	+ 2.5
NO_3	−274.5	+17
$\frac{1}{2}Cl_2O$	− 47.5	+11
ClO	− 61	+27
$\frac{1}{2}Cl_2O_2$	− 62	+26
$\frac{1}{2}Cl_2O_3$	−110	+ 7.5
ClO_2	−121	+26
ClO_3	−179	+27
$\frac{1}{2}Cl_2O_6$	−180	+26
$\frac{1}{2}Cl_2O_7$	−204	+31.5
ClO_4	−200	+ 6.5

It is clear that the problem of the highest forms can be broken down to essentially two questions: one of these, which was solved at an early date by D.I. Mendeleev, is the question of the limiting forms possible from the viewpoint of the periodic law (normal forms); the other, which was also posed by D.I. Mendeleev, is the question of the forms which are attainable in practice and thermodynamically stable under ordinary conditions.

From the example just given, it follows that in the case of solid oxides, as in the case of gaseous substances, the low forms, as well as the high forms, are not always capable of existence. Thus osmium does not form Os_2O, OsO or Os_2O_3; ruthenium does not form Ru_2O or RuO, while the Ru_2O_3 described in the literature, prepared by careful dehydration of the corresponding hydroxide, is metastable at room temperature, like FeO, which, as is well known, is a substance capable of undergoing the reaction: $4FeO = Fe_3O_4 + Fe$ and which becomes truly stable only at temperatures above 570°.

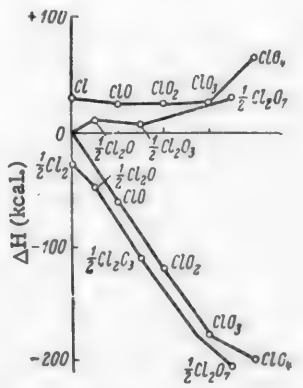
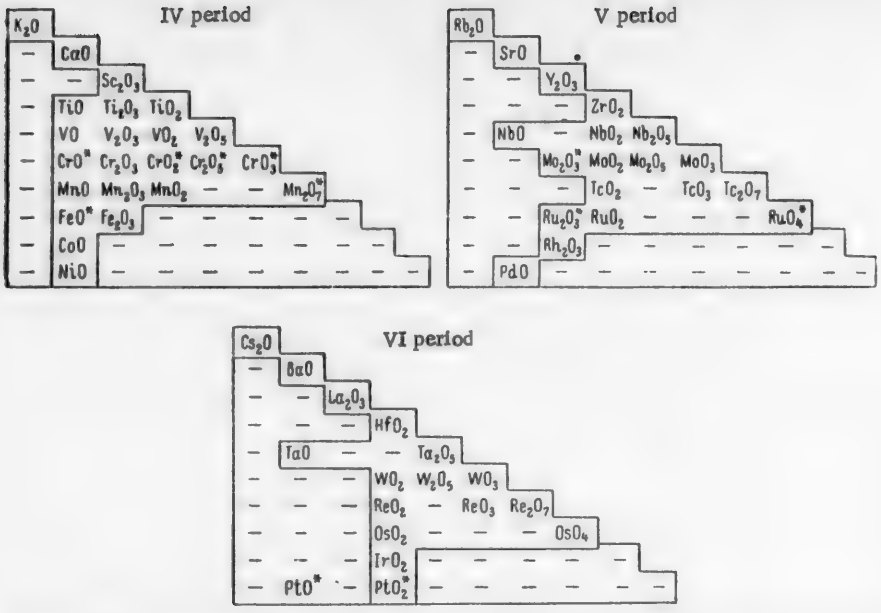


Fig. 5. The energies of formation of the oxides of chlorine from the free atoms (lower curves) and from the simple substances (upper curves).

The idea of the existence of two limits (an upper and a lower) in the series of stable compounds (for example, oxides) formed by an element has been particularly clearly formulated by A.A. Baikov [3], who by so doing took a further step in the development of the work of D.I. Mendeleev on per- and sub-compounds. As an illustration of the general applicability of this idea we give below lists of the oxides formed by the elements of the even series of periods IV – VI of the periodic system.

The asterisks denote metastable substances, while the vacant spaces correspond to compounds which are not found in practice in the free condensed state in macroscopic quantities. As can be seen from the data presented, whole series of both lower and higher oxides are so unstable that they are missing from the list of substances known to chemistry. In addition, in the case of certain elements gaps exist where different degrees of oxidation are missing within a series. Thus in the case of niobium Nb_2O_3 is missing, in the case of tantalum Ta_2O_3 and TaO_2, and in the case of osmium Os_2O_5, OsO_3 and Os_2O_7,* are missing.

*In order to simplify the discussion at this stage we have not taken into account oxides of variable composition or oxides of intermediate type such as Mn_3O_4, Fe_3O_4, Co_3O_4, Pb_3O_4.



When we consider that the fact that these various oxides have not been found cannot, in the majority of cases, with the present-day position of science, be attributed to lack of study, chance failure, or the shortcomings of synthetic methods, it is natural to conclude that there exists a real law which prohibits the existence of certain compounds. The prohibition, of course, is not absolute, but is related in some fashion to the thermodynamic instability of the compounds in question, which is determined in turn by their specific chemical character. Attempts to explain the existence or nonexistence of various chemical compounds using thermodynamic theories and from the point of view of energy characteristics in particular, have been justified long ago, as is well known. We have only to recall the ideas put forward on this question approximately 30 years ago by Grimm [4], who calculated the approximate energies required for the formation of such imaginary compounds as the chlorides of the inert gases or nonexistent compounds such as $MgCl_3$, $AlCl_4$, etc.

Let us examine the oxides formed by the elements of the even series in the long periods of the periodic system, in order to find, on the basis of a concrete example, exactly what new features are introduced when we go from gaseous compounds to crystalline structures.

For the series of elements: K-Fe, Rb-Ru, Cs-Os, the somewhat schematic Figure 6 shows groups of curves, starting from the origin, and representing the energies of formation of the gaseous oxides from the free atoms; the curves starting from points corresponding to the energies of atomization of 1 g-atom of the metal provide information regarding the energies of formation of the same gaseous oxides from the simple substances.

If we examine Figure 6 in more detail, we see that the change from atoms to the simple substances, by raising the curves, causes a considerable number of the points (for example, almost all the points for Fe, Ru, and Os) to be transferred to the endothermic region, and this as in the case of the oxides of nitrogen and chlorine, is related principally to the high energies of sublimation of the metals; the curves, however, still remain regular, i.e., there is still no tendency for the saturation limit to be shifted from the normal degree of saturation to some other lower degree of saturation. Since the energies of sublimation of the metals increase considerably as we go from period IV to periods V and VI of the system, the field occupied by the figurative points in the endothermic region will be greatest in period VI.

For the sake of clarity we give below the values for the energies of atomization of the simple substances which we have used in the construction of Figure 6; all the values are calculated for 1 g-atom. The figures given

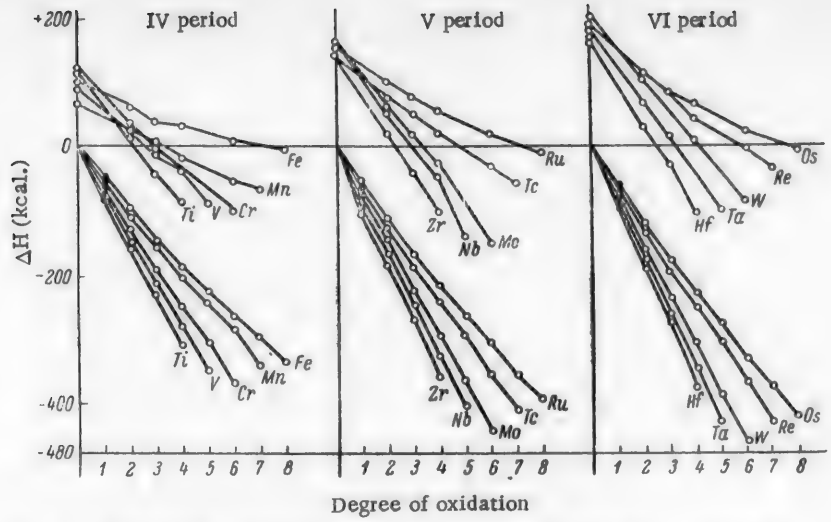


Fig. 6. The energies of formation of gaseous oxides (calculated for 1 g-atom of metal) from the free atoms (lower group of curves) and from the simple substances (upper group of lines).

in brackets are less reliable than the others, for which a number of new determinations have recently been made [2].

K	Ca	Sc	Ti	V	Cr	Mn	Fe
21.5	42.6	93	113	122	93	68	99
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru
20.5	39	(100)	142	162	156	(143)	(154)
Cs	Ba	La	Hf	Ta	W	Re	Os
19	42	88	(160)	(185)	202	189	174

Table 6 gives values for ΔH of formation of the gaseous molecules from the atoms, which we have also used [5] (in some cases for diatomic molecules spectral data are given, but in the majority of cases the values are calculated or interpolated using the thermal effects of oxide formation, from their heats of sublimation and from the energies of atomization of the simple substances).

We see from a comparison of the values of ΔH for periods IV, V and VI that Fig. 6 provides a good illustration of the periodicity which is a feature of the system of the elements. At the same time, in addition to the repetition in each period of similar geometrical characteristics, we also observe in the graphs a certain regularity in the course of the change in the quantitative expressions of these characteristics (which assists in interpolation). In effect, the original curves for ΔH for the gaseous oxides and atoms fall lower and lower as we change from period IV to period VI. Within the limits of the separate periods, we observe a lowering of the points on the same curves on going from the alkali metal to Cr, Mo and W, followed by a raising of the points after the elements of Group VI (according to a law governing movement along a horizontal row of the system, and not within a vertical column). Both these features are related to the interpretation of Bayley's rules [6], which were discussed by D.I. Mendeleev in his "Principles of Chemistry."

Figure 7 shows the change observed on going from the energies of formation of the gaseous oxides from the simple substances (upper curves) to the standard energies of formation of the solid oxides from the simple substances (lower curves), i.e., taking account of the energies of condensation.

As might have been expected, the curves showing the standard ΔH of formation in Fig. 7 lie below the original curves corresponding to the gaseous oxides, by virtue of the evolution of the energy of condensation.

TABLE 6

	Value of ΔH for the degree of oxidation							
	1	2	3	4	5	6	7	8
				IV period				
K	—39							
Ca		—104						
Sc		—138	—206.5					
Ti		—160	—236	—318				
V		—146	—217	—284	—355			
Cr		—130	—192	—252	—312	—371		
Mn		—106	—155	—203	—250	—297	—342	
Fe		— 98	—144	—186	—227	—267	—305	—339
				V period				
Rb	—29.5							
Sr		—111						
Y		—162	—243					
Zr		—184	—275	—365				
Nb		—168	—250	—330	—410			
Mo		—154	—229	—301	—373	—445		
Tc		—126	—186	—244	—301	—358	—410	
Ru		—112	—165	—216	—265	—313	—358	—397
				VI period				
Cs	— 9							
Ba		—126						
La		—161	—241.5					
Hf		—192	—277	—380				
Ta		—176	—263	—347	—431			
W		—160	—238	—314	—390	—465		
Re		—130	—193	—253	—313	—372	—430	
Os		—118	—174	—228	—282	—334	—376	—419

The most characteristic feature of the standard curves is the sharp change in their shape, which in the case of iron and manganese leads to the appearance of minima at the Fe_2O_3 and MnO_2 points, i.e., the highest, limiting, stable compounds.

To assist in a more detailed examination of Fig. 7, the numerical values for the data used in its construction [5] are given in Table 7.

Table 8 gives values for the energies of condensation of the oxides of the elements of periods IV-VI, although these values in a number of cases have no claim to accuracy, and in a number of cases even represent a certain degree of fiction, since by no means all of the oxides which are of interest to us (for example, oxides of the type M_2O_3 and M_2O_5) are stable in the gaseous state; some of them are polymerized in the vapor state.

Similarly Table 9 gives values for the energies of formation of the gaseous oxides from the simple substances.

When we examine the influence of the energy of condensation on the properties of the oxides, we should pay particular attention to the high values of these energies, which are often considerably greater than 100 kcal., i.e., they are reaching values of the same order as the energies of atomization of the solid metals. This fact is important not only in connection with the question of what it is that makes many endothermic gaseous oxides exothermic and stable in the solid state, but also in connection with the fact that the stabilization brought about by the energy of condensation often constitutes the whole or almost the whole of the exothermic effect of formation of the solid oxide. Thus, for example, if CaO were unable to form a crystalline structure at room temperature and were gaseous, its energy of formation would be of the order of -2 kcal.; the very high energy of condensation, equal to -150 kcal., is added to the -2 kcal., and gives a thermal effect of -152 kcal., as a result of which calcium oxide is very stable. The gaseous oxides MnO and FeO, which are characterized by endothermic

formation effects equal to +21 and +60 kcal, respectively, might have behaved as explosive substances: they are in fact stabilized by their energies of condensation, equal to 113 and 123 kcal. Oxides such as UO_2 and OsO_2 in the gaseous state would have endothermic heats of formation from the simple substances equal to +57 and +64 kcal., but their condensation energies, which are equal to 110 and 126 kcal, respectively, make them quite stable. The oxides of the alkali metals are likewise stable only by virtue of their condensed state.

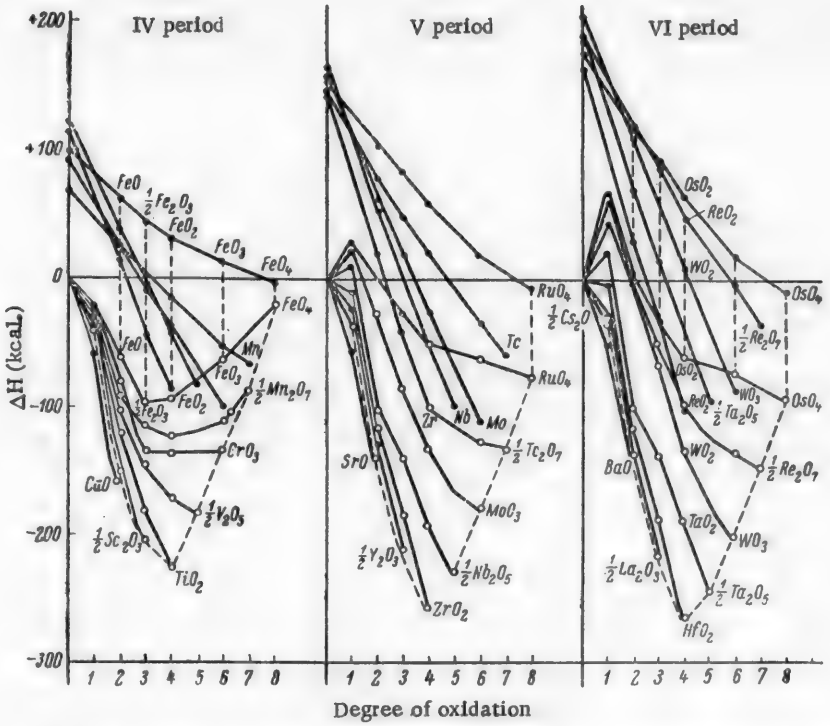


Fig. 7. The energies of formation of oxides (calculated for 1 g-atom of metal) from the simple substances.

Explanation in the text.

It is thus clear that the idea put forward persistently by D.I. Mendeleev, concerning the superposition of what were in the past called "physical" factors, for example, changes in states of aggregation, on purely chemical interactions, plays more than a secondary role in determining the fate and behavior of chemical compounds. It is of course not difficult to see what a decisive importance the energies of condensation will have in the formation of refractory and nonvolatile substances, such as the oxides, carbides, nitrides, etc.; more volatile compounds, the chlorides for example, will be dependent to a lesser extent on the condensation energies, but nevertheless these energies will play a part of no small importance in the case of the chlorides also.

It is also clear that the values of the condensation energies themselves depend on the structure of the crystals, on the change in coordination numbers on going from the molecules to the crystals, on the nature of the forces joining the atoms and ions, on the dimensions and polarizability of the atoms, and on many other factors, which are not always fully characterized by the term "physical" factor.

From a detailed examination of Table 8 we see that the smallest values of the quantity in question correspond to the 1st, 6th, 7th and 8th degrees of oxidation. A maximum condensation energy value, characteristic of the oxide series for a given element, is usually found to correspond to one of the degrees of oxidation lying between the 2nd and 4th. In periods V and VI this maximum is most often found to correspond to the 4th degree of oxidation; in period IV it is most often found to correspond to the 3rd degree of oxidation.

This phenomenon is evidently related to the particular features of the crystal structures of the individual chemical forms (M_2O_3, MO_2) and to the nature of the chemical bonds.

As a result of the existence of a maximum in the series of condensation energies corresponding to the different degrees of oxidation of a given element, the regular ΔH of formation curves for the gaseous oxides acquire important new features – minimum points and points of inflection (in the case of OsO_2, for example), which have an important influence on the chemical characteristics of the series of compounds. This influence is reflected both in the position of the upper and lower limits of stability in the series, and in the appearance of gaps corresponding to individual degrees of oxidation within the stable region of the series. This influence is particularly apparent in the case of the oxides of iron, manganese and chromium where, as a result of the low

TABLE 7

	Values of $\Delta H_{stand.}$ (for 1 atom of metal) for the degree of oxidation							
	1	2	3	4	5	6	7	8
				IV period				
K	—43.2							
Ca	—	—152						
Sc	—	—	—205.5					
Ti	—	—122	—182	—226				
V	—	—103	—148	—171	—186			
Cr	—	(— 82)	—136.5	—138	—	—138		
Mn	—	— 92	—115	—124	—	(—111)	— 89	
Fe	—	— 63	— 98.5	— 95	—	(— 65)	—	(—25)
				V period				
Rb	—39.5							
Sr	—	—141						
Y	—	—	—210					
Zr	—	(—118)	(—185)	—259				
Nb	—	(—102)	(—142)	—194	—227.5			
Mo	—	(— 30)	(— 88)	—133.5	—	—180		
Tc	—	—	(— 67)	—103	—	—128	—133	
Ru	—	—	—	— 53	—	— 65	—	—77
				VI period				
Cs	—38							
Ba	—	—133						
La	—	—	—217.5					
Hf	—	(—119)	(—190)	—266				
Ta	—	(—101)	(—140)	(—190)	—244.5			
W	—	—	(— 68.5)	—136	—	—201		
Re	—	—	(— 49)	—102	—	—138	—148	
Os	—	—	—	— 62	—	— 75	—	—93.6

condensation energies, the oxides FeO_4, FeO_3, FeO_2, Mn_2O_7, MnO_3 are unstable and dissociate exothermically to form Fe_2O_3 and MnO_2; in the case of chromium, the oxide CrO_3 has the properties of a powerful oxidizing agent, while CrO_2 is a compound which is even difficult to prepare.

A study of Figure 7 enables us to understand the meaning of the Bayley rule, in which D.I. Mendeleev was interested. His "Principles of Chemistry" gives an example illustrating this rule, which states that the thermal stabilities of the highest oxides of the elements of the even series increase as we go from top to bottom of a vertical group in the periodic system; thus, WO_3 is more difficult to decompose by heating than MoO_3, which is in turn more stable than CrO_3.

The same rule is of course applicable to TiO_2, ZrO_2 and HfO_2; to Ta_2O_5, Nb_2O_5 and V_2O_5; to Re_2O_7, Tc_2O_7 and Mn_2O_7 and to OsO_4, RuO_4 and FeO_4.

The Bayley rule is illustrated in Fig. 7 by the sloping lines joining the points for the ΔH of formation of, for example, CrO_3, MoO_3 and WO_3.

It is now possible to characterize the Bayley rule [6] quantitatively and indicate the principle thermodynamic features which make it applicable; two such features can be recognized.

TABLE 8

	Values for energy of condensation (in kcal.) for degree of oxidation							
	1	2	3	4	5	6	7	8
				IV period				
K	54							
Ca	—	150						
Sc	—	—	182					
Ti	—	134	136	139				
V	—	138	142	130	100			
Cr	—	(104)	126	97	—	37		
Mn	—	113	117	107	—	(55)	21	
Fe	—	123	142	126	—	(74)	—	(21)
				V period				
Rb	56							
Sr	—	128						
Y	—	—	156					
Zr	—	(135)	(140)	154				
Nb	—	(155)	—	144	128			
Mo	—	(91)	(104)	107	—	68		
Tc	—	—	—	123	—	92	73	
Ru	—	—	—	110	—	83	—	70
				VI period				
Cs	58							
Ba	—	108						
La	—	—	153					
Hf	—	(146)	(161)	164				
Ta	—	(169)	(150)	—	147			
W	—	—	—	142	—	114		
Re	—	—	—	147	—	132	112	
Os	—	—	—	126	—	92	—	85

1) The increase [7] in the condensation energies of the highest oxides as we move down the system:

TiO_2	$^1/_2V_2O_5$	CrO_3	$^1/_2Mn_2O_7$	FeO_4
139	100	37	21	21
ZrO_2	$^1/_2Nb_2O_5$	MoO_3	$^1/_2Tc_2O_7$	RuO_4
154	128	68	73	70
HfO_2	$^1/_2Ta_2O_5$	WO_3	$^1/_2Re_2O_7$	OsO_4
164	147	114	112	85

This increase displaces the figurative points for the solid oxides in Fig. 7 downwards and makes the highest oxides more stable both relative to the lower oxides of the same element and also relative to the highest oxides of an element standing nearer the beginning of the system in the same vertical group.

2) The steeper shape of the bond energy curves for the gaseous molecules of elements situated low in the periodic system (this can be seen from Fig. 6); this shape results in compensation for the increase in the atomization energy of the metal, so that the points for FeO_4, RuO_4 and OsO_4, for example, on the ΔH of formation curves for the gases from the simple substances lie approximately on the same ordinate.

Science has still to reach a deeper understanding of the Bayley rule; indeed we still do not know just why the condensation energies in the series CrO_3, MoO_3, and WO_3 increase, and why they do so with such rapidity;

we likewise do not know why the bond energies in the gaseous molecules of the same substances, formed from the atoms, increase as we go from Cr to Mo and W.

TiO_2	$^1/_2V_2O_5$	CrO_3	$^1/_2Mn_2O_7$	FeO_4
—318	—355	—371	—342	—339
ZrO_2	$^1/_2Nb_2O_5$	MoO_3	$^1/_2Tc_2O_7$	RuO_4
—365	—410	—445	—410	—397
HfO_2	$^1/_2Ta_2O_5$	WO_3	$^1/_2Re_2O_7$	OsO_4
—380	—431	—465	—430	—419

Thus the shift of the upper limit in the oxide series for the period IV elements under discussion depends on the reduction in the condensation energies for high degrees of oxidation, while the nonappearance of this shift

TABLE 9

	Values for the energies of formation of gaseous oxides from the simple substances (in kcal.) for the degree of oxidation							
	1	2	3	4	5	6	7	8
	IV period							
K	+11							
Ca	—	— 2						
Sc	—	—	—24					
Ti	—	+ 12	—46	— 87				
V	—	+ 35	— 6	— 44	— 86			
Cr	—	+ 22	—10	— 41	—	—101		
Mn	—	+ 21	+ 2	— 17	—	— 56	—68	
Fe	—	+ 60	+ 43	+ 31	—	+ 9	—	—4
	V period							
Rb	+16							
Sr	—	— 13						
Y	—	— 5	—54					
Zr	—	+ 17	—45	—105				
Nb	—	+ 53	—	— 50	—100			
Mo	—	+ 61	+16	— 27	—	—112		
Tc	—	+ 76	+ 46	+ 19	—	— 36	—60	
Ru	—	+101	+ 77	+ 57	—	+ 18	—	—7
	VI period							
Cs	+20							
Ba	—	— 25						
La	—	— 14	—65					
Hf	—	+ 27	—29	—102				
Ta	—	+ 68	+10	—	— 98			
W	—	+101	—	+ 6	—	— 87		
Re	—	+118	+ 85	+ 45	—	— 6	—36	
Os	—	+115	+ 89	+ 64	—	+ 17	—	—9

in the case of elements from periods V and VI is related to the less sharp change on going from the condensation energies for the 4th degree of oxidation to the energies for higher degrees of oxidation.*

*It is undoubtedly true that the above-mentioned Bayley rules regarding the decrease in stability of the highest compounds of the elements in the odd series of the periodic system are related to the phenomenon of secondary periodicity.

It is now appropriate to consider the question of the rule relating to the shift of the lower limit. An examination of the list of stable oxides shows that the lower limit is shifted towards higher degrees of oxidation as we go from period IV to period V and even more as we go to period VI. Figure 7 reveals quite clearly the reason for this phenomenon: it is primarily due to the increase in the atomization energies of the metals, to the movement of ΔH, for many oxides corresponding to the 1st degree of oxidation, into the endothermic region (on the $\Delta H_{stand.}$ curves) and to the sharp approach of the remaining points corresponding to the 1st and 2nd, and sometimes also to the 3rd, degrees of oxidation, towards the zero ordinate, albeit in the exothermic region.

As a concrete example of this situation we may consider the oxides of osmium, of which only two are stable, OsO_2 and OsO_4 (Fig. 8). The lower oxides are not found as a result of the high atomization energy of osmium, and the consequent tendency for these oxides to break down exothermically to Os and OsO_2. The oxides intermediate between OsO_2 and OsO_4 also break down exothermically to form these two oxides. The reason for the phenomenon lies in the maximum value shown by the condensation energy of the oxide OsO_2.

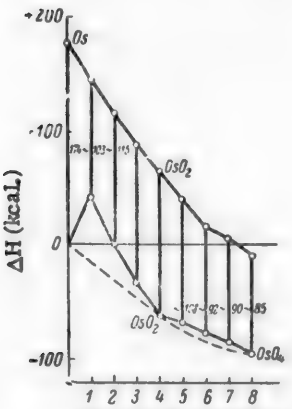


Fig. 8. The energies of formation of osmium oxides from the simple substances (upper curve for the gaseous oxides, lower curve for the condensed oxides).

Since the point for the compound Os_2O_3 lies above the straight line joining the OsO_2 point to the origin, Os_2O_3 is able to decompose exothermically to Os and OsO_2.

$$2Os_2O_3 - 54 = 3OsO_2 + Os$$

The particular favorable energy features of the OsO_2 crystal structure cause the point for this compound to be moved downward. If the line of points corresponding to the ΔH of formation for the gaseous oxides from the simple substances were not inclined so steeply as is actually the case for Os (period VI), but had a lower slope, like the lines for the oxides of iron (period IV), then the maximum condensation energy for OsO_2 might have resulted in the appearance of a minimum point on the ΔH curve for this oxide and thus determined the upper limit of the series. In the case of osmium, however, the minimum point for OsO_2 degenerates into a point of inflection: before OsO_2 the ΔH curve shows a convexity downward , while after OsO_2 it shows a convexity upward. As a result, the oxides intermediate between OsO_2 and OsO_4 have points which lie above the straight line joining the figurative OsO_3* and OsO_4 points; all these intermediate oxides therefore break down exothermically, for example

$$2OsO_3 - 6 = OsO_2 + OsO_4$$

Thus the particularly high condensation energy of OsO_2 leads, as it were, to the absorption by this compound of its neighbors in the series. It can be seen from this example that the importance of the heats of condensation of the oxides is considerable not only in connection with the shift of the upper limit of the series, but also in connection with the lower limit and the nonappearance of certain oxides within the series. In general the magnitude of the condensation energy of the free metal is reflected in a shift of the lower limit and in an overall reduction in the thermal stability of all the compounds of the element in question.

Thus the question of whether a given element, in combination with a second element, will give rise to few or many chemical forms (degrees of oxidation) depends not only on the number of electrons in the outer electron cloud of the atom (the number related to the group number of the element), but also on the chemical nature of the second element, or partner, on the energy of atomization, and sometimes also on the energy of ionization, of both partners, and also on the condensation energy of the compounds obtained. In resolving this problem of the stability of a particular form it is not at all sufficient to study that form in isolation: it is always necessary to study all the possible forms and the competition between them. In addition, of course, it is necessary to change from ΔH curves to ΔF curves, i.e., to take into account the values of $T\Delta S$. This can be readily done when the effect of temperature is taken into account.

*As in original – Publisher's note.

It is undoubtedly true that, in solutions, the part of the condensation energy is taken by the solvation energies, by the energies of all the possible rearrangements in the structure of the molecules under study (precipitation, electrolytic dissociation, complex-formation, protolytic processes, polymerization, disproportionation), and also by the energy of the more intensive chemical processes taking place between the solvent and the dissolved substance (hydrolysis, the formation of oxy-ions, oxidation and reduction).

SUMMARY

1. The thermodynamic range of existence of a particular degree of oxidation for a given element depends on the statistical thermodynamic competition between the compound in question, the corresponding simple substances, and also the compounds of different degrees of oxidation, i.e., it is a characteristic which is necessarily dependent on the interrelationship between the members of the whole series of binary compounds which may be formed by the two simple substances.

2. The characteristic thermodynamic features of a series of stable compounds lead to the thesis that there exists an upper and a lower limit for the series, these limits corresponding to the formation of compounds saturated with the first or the second component; supersaturated compounds lying on either side of these limits disproportionate with the formation of the corresponding simple substance. Gaps may also exist within the stable limits, since individual states may break down by the exothermal decomposition of the compounds corresponding to these states into neighboring substances bordering the gap.

3. From an examination of the gaseous oxide series, it can be seen that high energies of atomization for the simple substances narrow the stability range in the oxide series for a given element.

4. In the breakdown of individual states of oxidation the question of whether the molecules are odd or even is significant, as is the phenomenon of polymerization of the compounds.

5. It has been shown that a considerable number of oxides formed by all the metals in the even series of the long periods of the periodic system are unstable in the gaseous state and dissociate: the lower oxides dissociate to the simple substances, while oxides of high degree of oxidation dissociate into oxygen and oxides of medium degree of oxidation (at high temperatures, where $T\Delta S$ plays an important role). The question of the gaseous oxides is complicated by the fact that in many cases we do not know the exact forms in which the various oxides exist in the vapor state.

6. In the case of the condensed oxides, an extremely important part is played by the enthalpies of condensation, which have maximum values for compounds of medium degrees of oxidation (4th or 5th degree in most cases). In period IV of the periodic system this feature in a number of cases leads to the formation of a minimum on the enthalpy curves, thereby creating conditions which lead to a reduction of the upper limit of stability to a state considerably lower than that corresponding to the group number. The fact that the decrease in the enthalpies of condensation of the highest oxides of the elements of periods V and, more especially, VI is less sharp than in period IV leads to the situation where the highest oxides of Tc, Ru, Re and Os are stabilized and there is then no minimum on the enthalpy of formation curves for the oxide series of these elements.

7. The well known Bayley rule concerning the shift of the upper limit of a series towards higher degrees of oxidation, i.e., the stabilization of the higher oxides, for d-metals, when we move from below upwards within the vertical groups of the periodic system, are explained in the light of the phenomena of the increase in the condensation energies of the highest oxides and the decrease in the endothermic effect of the gradual saturation of the metal atoms by oxygen.

8. A new rule has been pointed out concerning the shift of the lower limit in the series to higher degrees of oxidation as we move from above downwards within a group of the system. This rule is explained by the shape of the metal atomization energy curves.

9. In the region of the oxide with the highest condensation energy (for example, OsO_2), there arises a tendency for the neighboring oxides of higher and lower degrees of oxidation to disappear from the series as a result of disproportionation.

10. Analogous conclusions are also applicable to the explanation of the stability of individual degrees of oxidation in a wider sense, i.e., in the application of the above rules not only to oxides, but also to compounds of other types, and also to compounds in solution.

11. Certain analogies may also be pointed out with the characterization of the isotopic series of individual elements.

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NUCLEAR (ATOMIC) CONCENTRATION AND SPECIFIC GRAVITIES OF HYDROCARBONS

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The value of the nuclear (atomic) concentration (NC) is determined by the total number of atoms of the original elements in the composition of a given substance, in a 1 liter volume,

$$NC = AN \text{ atoms} \quad (1)$$

where A is the nuclear concentration index and N is Avogadro's number.

In the case where the chemical formula of the substance has been determined (either rationally or empirically), the value of the nuclear concentration index is determined by the equation

$$A = 1000 \frac{nd}{M}, \quad (2)$$

where n is the number of atoms in a molecule, d is the specific gravity and M is the molecular weight.

We should note here that the value of the nuclear concentration index is very closely and obviously related to the concept of the average volume of an atom in complex bodies, introduced into science by D.I. Mendeleev [1]. The smaller the Mendeleev average atomic volume, the higher the value of A and the reverse.

In order to achieve a greater measure of objectivity the following calculations are based on literature data collected in one of the newest fundamental reference books [2].

If all the solid and liquid hydrocarbons listed in [2] which have been sufficiently investigated at a temperature as close as possible to + 20°, are sorted into groups by the increasing numbers of hydrogen atoms in the composition of one molecule, we will obtain a series of groups with the compositions C_XH_6, C_XH_8, C_XH_{10} etc. (Table).

Average Value of the Nuclear Concentration Index A_{av} of Hydrocarbons at + 20° According to Data in [2].

Formula	No. of compounds	A_{av}	Formula	No. of compounds	A_{av}
C_xH_6	14	128.4	C_xH_{20}	41	167.2
C_xH_8	26	137.7	C_xH_{22}	22	165.5
C_xH_{10}	63	145.5	C_xH_{24}	33	172.9
C_xH_{12}	87	151.3	C_xH_{26}	1	168.0
C_xH_{14}	109	155.6	C_xH_{28}	4	170.5
C_xH_{16}	153	161.4	C_xH_{30}	6	167.9
C_xH_{18}	89	164.6	C_xH_{32}	8	173.7

A full picture of the dispersion of separate points, corresponding to the calculated individual values of A for the separate members of a group may be drawn up for each of these groups and the value and character of the deviations from A_{av} that are observed may be evaluated quantitatively.

For this purpose we sorted all the 656 hydrocarbons, on which data is given in [2], into different groups and tabulated the data on the number of compounds in each separate group.

One may conclude from the data in this table that the average values calculated for the nuclear concentration index A_{av} and, consequently, the average values calculated for the nuclear concentration of hydrocarbons NC_{av}, increase smoothly and at a gradually decreasing rate with an increase in the number of hydrogen atoms in one molecule [3].

Then naturally a problem arises on the extent of dispersion of the A values and the number of substantial deviations from A_{av}. Of the 656 hydrocarbons, 610 compounds, or 93.0%, are characterized by values of the nuclear concentration index that differ by not more than 6% from the average values. Only 34 hydrocarbons, or 5.2% of the total number, have individual values for the nuclear concentration index A which exceed A_{av} by more than 6%. Five hydrocarbons in this group have unknown chemical structure while the remaining 29 compounds are either alicyclic compounds, i.e., are characterized by the presence of closed carbon atom chains, or are derivatives of naphthalene, anthracene and phenanthrene, i.e., they have condensed aromatic nuclei. Finally, 12 hydrocarbons, or 1.8% of the total number, are characterized by extremely low individual values for the nuclear concentration index. They are all unsaturated compounds of the aliphatic series.

In this way, an analysis of the factual material in [2] leads us to a second, important conclusion: at temperatures close to + 20° the great majority of hydrocarbons are characterized by values of the nuclear concentration index A that do not differ by more than 6% from the average calculated value of A_{av}. The relatively few deviations observed that were more than 6% over A_{av} have a regular character.

The temperatures at which the specific gravities given in [2] were determined are often far from + 20°. However, a difference of 10° in the temperature of liquid organic substances often causes a deviation of several percent in the nuclear concentration index A. Further, one should take into account the fact that the specific gravities given in the literature were determined by different experimenters at various times, by various methods and using preparations of differing origin and purity. Therefore, reference books often give specific gravities which differ by several percent even for the same substance at the same temperature. Finally, we are dealing here with two different aggregate states of material. At +20° about half of all the hydrocarbons given in [2] are in the liquid and the rest are in the solid state. Considering the above it is most remarkable that the great majority of the hydrocarbons described in the literature have values for nuclear concentration that fit within the rather rigid limits assigned by us.

The conclusions formulated above have more than theoretical interest. They may be applied in determining the molecular weights and chemical structures of hydrocarbons. Also this opens up the possibility of defining a regular relation between the composition and structure of hydrocarbons, on the one hand, and some of their chemical and physical properties, on the other. Let us consider the latter problem in more detail.

It follows from equation (2) that it is possible to establish unequivocally the specific gravity of any hydrocarbon of a given chemical composition if the value of its nuclear concentration index A is first known. Using the average values A_{av} given in the table for hydrocarbons containing from 6 to 32 hydrogen atoms in one molecule, we can establish by calculation the corresponding average specific gravities of all the diverse hydrocarbons with this composition, containing any number of carbon atoms, as found practically, in one molecule.

We calculated the average specific gravity at + 20° for a large number of hydrocarbons with the composition C_xH_z, where $\underline{x}$ varied from 2 to 26 and $\underline{z}$ from 6 to 32.

Of the total 656 hydrocarbons which, according to the data in [2], have this chemical composition, 618 compounds, or 94.2%, are characterized at + 20° by values of specific gravity which differ by not more than 0.05 from those calculated from A_{av}. Only 33 hydrocarbons (5.0%) have at 20° specific gravities which differ by 0.06 – 0.10 from the average value. Finally, only five hydrocarbons (0.8%) are given specific gravities in [2] which differ from the calculated specific gravities d_{av} by more than 0.10. The high values of specific gravity are characteristic of alicyclic hydrocarbons and hydrocarbons with condensed benzene nuclei. The low values of specific gravity are those of unsaturated compounds of the aliphatic series.

Thus, a study of the extensive factual material accumulated in the literature on hydrocarbons indicates that the combination of the observed nuclear concentrations and specific gravities of hydrocarbons may be represented in the form of a single, orderly system, which is closely related to the composition and structure of the substance.

SUMMARY

1. The value of the nuclear (atomic) concentration of solid and liquid substances (NC) is determined by the total number of atoms of the original elements, in the composition of the given substance, in a 1 liter volume.

2. The calculated average NC values of hydrocarbons increase regularly in the direction of greater numbers of hydrogen atoms in the composition of one molecule.

3. The great majority of hydrocarbons are characterized at temperatures close to + 20° by NC values which do not differ by more than 6% from the calculated average NC values. The deviations over 6% observed had a strictly regular character.

4. A study of extensive factual material indicated that not only the NC values, but also the specific gravities of hydrocarbons are closely related to their composition and structure.

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THE VISCOSITY OF BINARY SYSTEMS WITH EXCHANGE INTERACTION

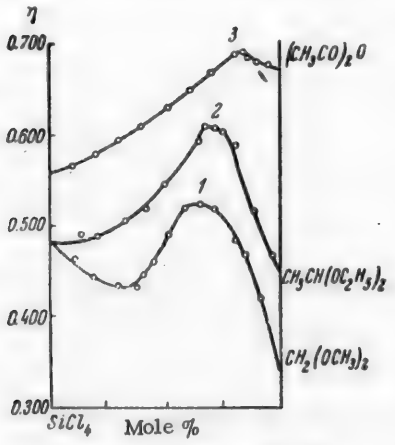
V.V. Udovenko and Iu.Ia. Fialkov

The viscosity diagrams of binary systems have been considerably systematized at the present time and are widely used for determining the character of the processes occurring. In the case of systems with chemical interaction, the existing classification [1] provides a type of diagram for systems in which the chemical reactions proceed with a decrease in the number of molecules, for example in the water – chloral system, or for systems in which the number of molecules remains the same, for example in the acetic anhydride – water system. As very few systems of the latter type have been studied, N.A. Trifonov proposed to investigate model systems such as diethyl ether – water, which could give an idea of the type of viscosity diagram for a system in which one chemical compound is formed without a change in the number of molecules.

It should be noted that in the acetic anhydride – water system the number of molecules does not change as a result of the chemical reaction as two molecules of acetic acid are formed from one molecule each of acetic anhydride and water. Reactions which proceed without a change in the number of molecules have possibilities other than the formation of only one chemical compound. Exchange interaction which results in two chemical compounds is not less widespread. This type of system is of considerable interest for the theory of physicochemical analysis but as yet no one has studied it by the viscosity method.

Data are given below on the viscosity of systems in which one of the components is silicon tetrachloride and the other is one of the following: methylal (dimethoxymethane), acetal (1,1-diethoxyethane) or acetic anhydride.

The silicon tetrachloride – methylal system



Viscosity isotherms at 20°
1. silicon tetrachloride – methylal
2. silicon tetrachloride – acetal
3. silicon tetrachloride – acetic anhydride, with benzene as solvent.

The silicon tetrachloride was purified in the same way as described in our previous work [2]. The procedure is also given there. Methylal was dried over potassium carbonate and distilled. The fraction with b.p. 41.5 – 42° (749 mm) was used in the work.

There was noticeable evolution of heat when silicon tetrachloride was combined with methylal. Measurements were taken a day after the mixture was prepared as the viscosity of the mixture changed for a certain period after the mixture was prepared. The experimental data on viscosity and density of this system at 20 and 30° are given in Table 1. The figure (curve 1) shows the viscosity isotherm of the silicon tetrachloride – methylal system at 20°. As the figure shows, the isotherm has a maximum in the region of 67 mole % of methylal which according to the generally accepted concepts on viscosity diagrams, should correspond to the formation of a molecular compound with a composition of 1 : 2. However, our previous investigations [2] had established that silicon tetrachloride did not form addition products with oxygen-containing organic substances. Consequently, the chemical reaction in this system is of a different character.

A mixture of silicon tetrachloride and methylal in a ratio of 1 : 2 was distilled at 745.5 mm. Two main fractions distilled off and these boiled at 59 – 61° and 98 – 100°. The analysis carried out gave the following results.

1st fraction. Found %: Cl 44.0. CH_3OCH_2Cl. Calculated %: Cl 44.04.

2nd fraction. Found %: Si 17.2; Cl 43.85. $SiCl_2(OCH_3)_2$. Calculated %: Si 17.4; Cl 44.04.

Thus, both the boiling points [4] and the results of analysis of the fractions indicate that the formation of dichlorodimethoxysilane and chlorodimethyl ether occurs in the system by the scheme

$$SiCl_4 + 2CH_2(OCH_3)_2 = SiCl_2(OCH_3)_2 + 2CH_3OCH_2Cl$$

In this case the maximum on the viscosity isotherm corresponds to the stoichiometric ratio at which the components react.

TABLE 1

The Viscosity and Density of the Silicon Tetrachloride – Methylal System

Methylal content (in mole %)	Density		Viscosity (in centipoises)	
	20°	30°	20°	30°
0.00	1.485	1.466	0.482	0.442
9.89	1.438	1.420	0.463	0.419
19.06	1.398	1.381	0.449	0.412
28.79	1.351	1.337	0.439	0.402
36.82	1.302	1.296	0.437	0.405
39.33	1.290	1.277	0.446	0.410
44.24	1.279	1.263	0.459	0.414
51.06	1.233	1.210	0.490	0.428
59.60	1.194	1.181	0.540	0.458
65.89	1.148	1.136	0.542	0.472
70.83	1.120	1.108	0.515	0.461
79.84	1.052	1.031	0.483	0.434
84.77	1.018	1.005	0.466	0.414
90.26	0.975	0.967	0.419	0.369
100.0	0.859	0.848	0.336	0.304

The silicon tetrachloride – acetal system

The acetal was purified in the same way as methylal. A fraction which distilled at 102.7 – 103.3° (747 mm) was used for the work. In preparing the mixtures noticeably more evolution of heat was observed than for the mixtures with methylal.

As the viscosity changed for a certain time after the preparation of the mixtures, the measurements were carried out a day after their preparation. The experimental data on viscosity and density of the silicon tetrachloride – acetal system at 20, 30 and 40° are given in Table 2. The figure (curve 2) gives the viscosity isotherm at 20°.

The viscosity isotherms have a maximum in the region of 67 mole % of acetal; as in the case with methylal, this maximum indicates the interaction of the components by the equation

$$SiCl_4 + 2CH_3CH(OC_2H_5)_2 = SiCl_2(OC_2H_5)_2 + 2C_2H_5OCH(Cl)CH_3$$

To confirm this scheme, we distilled a 1 : 2 mixture of silicon tetrachloride with acetal. The distillation gave two fractions: the 1st boiled at 96 – 98° and the second at 136°. An analysis of the fractions gave the following results.

1st fraction. Found %:Cl 32.4. $C_2H_5OCHClCH_3$. Calculated %: Cl 32.66.
2nd fraction. Found %: Si 14.2; Cl 37.4. $SiCl_2(OC_2H_5)_2$. Calculated %: Si 14.8; Cl 37.5.

Thus, the first fraction corresponded to α-chlorethyl ether and the second to dichlorodiethoxysilane [3].

It should be noted that phosphorus pentachloride reacts with acetal in an analogous manner. Bachmann [4] found that when phosphorus pentachloride was added in small portions to acetal, a reaction occurred by the scheme

$$CH_3CH(OC_2H_5)_2 + PCl_5 = C_2H_5OCH(Cl)CH_3 + C_2H_5Cl + POCl_3$$

The reactions of silicon tetrachloride with methylal, acetal and similar compounds may be of interest as an extremely convenient method for the directed synthesis of dichlorodialkoxysilanes, which proceeds in almost a 100% yield.

TABLE 2

Viscosity and Density of the Silicon Tetrachloride – Acetal System

Acetal content (in mole %)	Density			Viscosity (in centipoises)		
	20°	30°	40°	20°	30°	40°
0.00	1.485	1.466	1.447	0.482	0.462	0 402
13.00	1.393	1.377	1.361	0.489	0.450	0.410
20.26	1.342	1.326	1.311	0.488	0.450	0.413
32.44	1.251	1.236	1.220	0.503	0.459	0.421
41.02	1.199	1.185	1.171	0.515	0.475	0.427
49.27	1.147	1.135	1.121	0.542	0.492	0.442
59.09	1.092	1.081	1.067	0.572	0.515	0.461
63.77	1.062	1.050	1.039	0.591	0.534	0.476
67.03	1.044	1.032	1.021	0.609	0.538	0.484
71.00	1.024	1.012	1.008	0.606	0.552	0.490
74.57	0.998	0.987	0.976	0.600	0.541	0.481
80.82	0.958	0.948	0.938	0.586	0.520	0.467
83.85	0.949	0.938	0.928	0.555	0.492	0.447
88.13	0.913	0.903	0.891	0.514	0.456	0.410
96.55	0.855	0.845	0.835	0.455	0.416	0.375
100.0	0.837	0.827	0.817	0.451	0.404	0.364

The silicon tetrachloride – acetic anhydride system in benzene

We previously [5] established that when mixed silicon tetrachloride and acetic anhydride reacted by the equation

$$SiCl_4 + 4(CH_3CO)_2O = Si(OOCCH_3)_4 + 4CH_3COCl$$

to form silicon tetraacetate crystals. An exchange reaction also occurred in this system but it could not be studied as a two-component system due to the precipitation of crystals. Therefore, the silicon tetrachloride – acetic anhydride system was studied in benzene as an inert solvent. For this purpose we prepared solutions corresponding to an isoconcentrate containing 74.50 mole % of benzene. To complete the reaction, once prepared, the mixtures were sealed in tubes and heated on a boiling water bath for 1 hour.

The results of determining viscosity and density of the silicon tetrachloride – acetic anhydride system in solutions, containing 74.50 mole % of benzene at 20° are given in Table 3.

The viscosity isotherms are given in the figure (curve 3). As the figure shows, a rather sharp maximum is almost exactly at 80 mole % of acetic anhydride, i.e., exactly at the ratio at which the components react.

The examples we give show that in systems in which an exchange reaction is considerably displaced towards the formation of end products, the maximum on the viscosity isotherms indicates the stoichiometric ratio of the substances reacting. A series of factors may affect the position of the maximum in such systems, namely,

the degree of the starting materials' reaction, their association, the relation of the viscosity magnitudes of all the substances participating in the reaction, etc. All these problems are being investigated further.

TABLE 3

Viscosity and Density of the Silicon Tetrachloride – Acetic Anhydride System in benzene at 20° (74.50 mole % of benzene isoconcentrate)

Acetic anhydride content (mole %)	Density	Viscosity (in centipoises)	Acetic anhydride content (mole %)	Density	Viscosity (in centipoises)
0.0	1.073	0.557	75.3	0.974	0.675
10.6	1.060	0.564	80.0	0.967	0.686
20.1	1.048	0.575	82.7	0.968	0.685
29.7	1.035	0.593	85.0	0.960	0.680
39.9	1.021	0.608	90.0	0.954	0.675
50.1	1.003	0.626	95.0	0.947	0.673
60.4	0.994	0.647	100.0	0.941	0.670
69.7	0.980	0.665			

SUMMARY

1. By means of the viscosity and density, we studied the binary systems silicon tetrachloride – methylal at 20 and 30°, silicon tetrachloride – acetal at 20, 30 and 40° and silicon tetrachloride – acetic anhydride in benzene, as an inert solvent, at 20°.

2. It was established that the maximum of the viscosity isotherms of systems in which an exchange reaction is considerably displaced towards the formation of end products, is at the stoichiometric ratio of the substances reacting.

3. It was established that silicon tetrachloride reacts with methylal to form dichlorodimethoxysilane and chlorodimethyl ether and it reacts with acetal to give dichlorodiethoxysilane and α-chlorodiethyl ether. These reactions are a new method for preparing dichlorodialkoxysilanes, which differs from existing methods in its high yield and purity of products.

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PHYSICOCHEMICAL ANALYSIS OF BINARY SYSTEMS FORMED BY PHENOL WITH ACETIC ACID AND ITS CHLORO DERIVATIVES

I.M. Bokhovkin and E.G. Veselkova

As is known, the introduction of chlorine into an acetic acid radical results in increased acidity and, consequently, in greater chemical reactivity with other components [1]. This hypothesis was confirmed by studying binary systems formed by urea and acetamide with acetic acid and its chloro derivatives [2 - 6].

The purpose of the present work was to investigate the reaction of phenol with acetic acid and its chloro derivatives in the liquid phase.

The procedure has been described previously [2 - 6]. The starting materials were purified: acetic acid by freezing and phenol, monochloroacetic and trichloroacetic acids by distillation.

The concentrations are expressed in molecular percent, the surface tension in dynes/cm and the viscosity in centipoises. The surface tension, viscosity and density of all the systems were studied at 50, 70 and 90°.

The phenol – acetic acid system. The fusion diagram of the system consists of two branches of crystallization of the pure components, which cross at the eutectic point at 41.5% phenol and a temperature of -15° [7]. This form of diagram indicates the absence of chemical reaction in the system. The surface tension isotherms also indicate the same (Table 1, Fig. 1) as they increase smoothly from acetic acid to phenol; the density isotherms (Table 2, Fig. 2) are similar to an additive line; the viscosity isotherms (Table 3, Fig. 2) bulge towards the composition axis.

The phenol – monochloroacetic acid system was investigated by means of its fusion [8]. There was no chemical reaction of the components. The eutectic point corresponds to 69.0% phenol and 16.5°. The surface tension (Table 4, Fig. 3), density (Table 5, Fig. 4) and viscosity isotherms (Table 6, Fig. 4) also do not indicate the formation of a compound in the homogeneous, molten medium. The surface tension isotherms bulge towards the composition axis.

TABLE 1

Surface Tension of the Phenol – Acetic Acid System

C_6H_5OH (mole %)	Surface tension			C_6H_5OH (mole %)	Surface tension		
	50°	70°	90°		50°	70°	90°
0	24.46	21.79	20.04	39.6	30.43	27.75	25.45
5.9	25.23	22.21	20.69	44.3	31.13	28.40	26.11
10.6	25.99	23.40	21.35	49.6	31.77	29.12	26.85
14.9	26.63	24.05	21.98	54.8	32.59	29.81	27.58
20.0	27.56	24.85	22.76	59.1	33.00	30.45	28.12
24.4	28.15	25.47	23.45	64.8	33.87	31.05	28.79
31.7	29.26	26.58	24.37	70.0	—	31.61	29.35
36.0	29.96	27.19	24.99	75.0	—	—	29.98

TABLE 2

Density of the Acetic Acid – Phenol System

C_6H_5OH (mole %)	Density		
	50°	70°	90°
10	1.037	1.015	0.990
20	1.035	1.021	0.998
30	1.045	1.026	1.002
40	1.051	1.028	1.011
50	1.052	1.032	1.012
60	1.053	1.034	1.015
70	1.053	1.043	1.016

TABLE 3

Viscosity of the Acetic Acid – Phenol System

C_6H_5OH (mole %)	Viscosity		
	50°	70°	90°
10	0.84	0.60	0.44
20	1.03	0.69	0.50
30	1.22	0.79	0.55
40	1.44	0.89	0.62
50	1.69	1.01	0.67
60	1.97	1.14	0.74
70	2.29	1.29	0.81

In contrast to the preceding system, the surface tension hardly changes with changes in the mixture's composition.

The density decreases in the system from monochloroacetic acid to phenol. This decrease in density proceeds along an almost additive line. The viscosity of the system increases from monochloroacetic acid to phenol. The slope of the viscosity isotherm is less in this system than in the acetic acid – phenol system due to the small difference in the viscosities of monochloroacetic acid and phenol. It is also noteworthy that the viscosity of the monochloroacetic acid – phenol system decreases by a factor of approximately three with an increase in temperature from 50 to 90°.

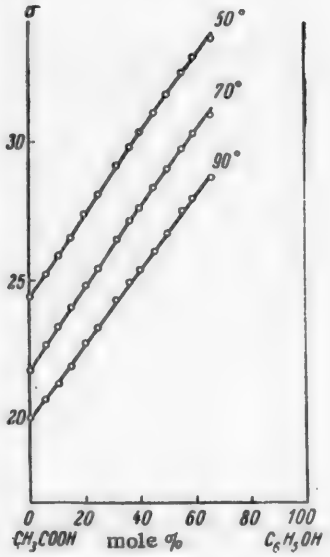

Fig. 1. Surface tension isotherms of the acetic acid – phenol system.

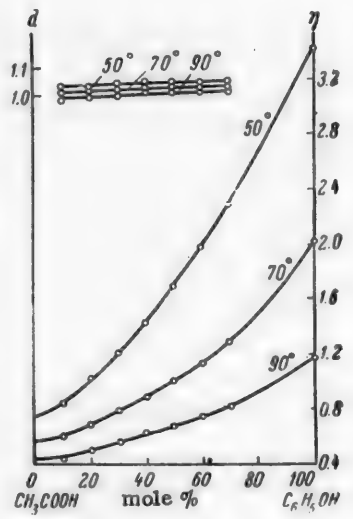

Fig. 2. Density (d) and viscosity (η) isotherms of the acetic acid – phenol system.

The phenol – trichloroacetic acid system. The chemical compound $C_6H_5OH \cdot CCl_3COOH$ was found in the system, which was studied by means of its fusion [8]. The fusion diagram shows this compound as a maximum (m.p. 37.50°). The surface tension (Table 7, Fig. 5) at 70 and 90° changes along an almost additive curve and increases smoothly from acetic acid to phenol. At 50° the isotherm deviates somewhat from

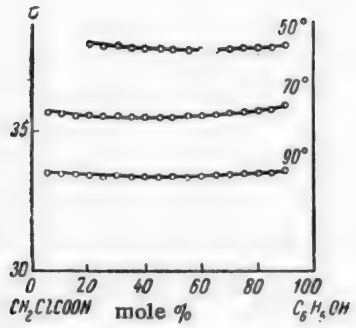

Fig. 3. Surface tension isotherms of the monochloroacetic acid – phenol system.

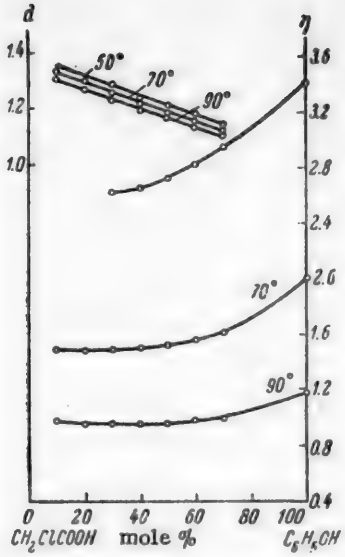

Fig. 4. Density (d) and viscosity (η) isotherms of the monochloroacetic acid – phenol system.

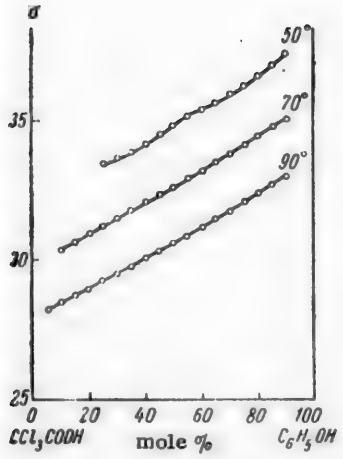

Fig. 5. Surface tension isotherms of the trichloroacetic acid – phenol system.

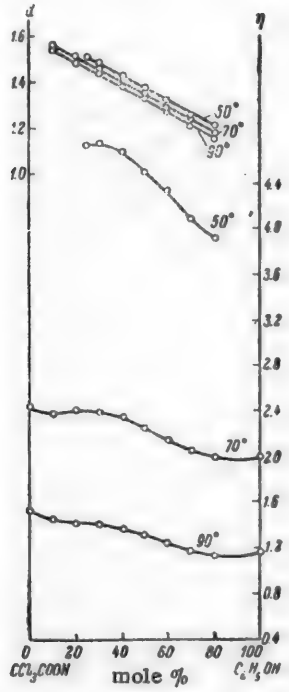

Fig. 6. Density (d) and viscosity (η) isotherms of the trichloroacetic acid – phenol system.

TABLE 4

Surface Tension of the Phenol – Monochloroacetic Acid System

C_6H_5OH (mole %)	Surface tension		
	50°	70°	90°
5	—	35.70	33.60
10	—	35.65	33.55
15	—	35.60	33.48
20	38.08	35.58	33.42
25	38.04	35.55	33.40
30	38.01	35.52	33.48
35	38.00	35.51	33.35
40	38.00	35.50	33.35
45	37.96	35.50	33.35
50	37.90	35.50	33.35
55	37.89	35.50	33.35
60	37.90	35.52	33.35
65	37.90	35.53	33.38
70	37.94	35.57	33.40
75	37.98	35.61	33.45
80	37.99	35.63	33.48
85	38.02	35.65	33.50
90	38.05	35.68	33.52

TABLE 5

Density of the Monochloroacetic Acid – Phenol System

C_6H_5OH (mole %)	Density		
	50°	70°	90°
10	—	1.339	1.309
20	—	1.301	1.267
30	1.282	1.256	1.231
40	1.244	1.219	1.196
50	1.208	1.182	1.168
60	1.177	1.154	1.133
70	1.144	1.120	1.108

TABLE 6

Viscosity of the Monochloroacetic acid – Phenol System

C_6H_5OH (mole %)	Viscosity		
	50°	70°	90°
10	—	1.49	0.97
20	—	1.49	0.95
30	2.63	1.48	0.95
40	2.66	1.50	0.95
50	2.74	1.52	0.96
60	2.84	1.56	0.97
70	2.96	1.62	0.99

TABLE 7

Surface Tension of the Phenol – Trichloroacetic acid system

C_6H_5OH (mole %)	Surface tension		
	50°	70°	90°
5	—	—	28.17
10	—	30.35	28.39
15	—	30.59	28.69
20	—	30.89	28.92
25	33.40	31.22	29.19
30	33.61	31.51	29.48
35	33.81	31.76	29.73
40	34.15	32.05	30.05
45	34.50	32.29	30.32
50	34.82	32.58	30.63
55	35.14	32.89	30.89
60	35.36	33.18	31.17
65	35.64	33.44	31.45
70	35.96	33.76	31.75
75	36.23	34.10	32.05
80	36.60	34.48	32.36
85	37.01	34.79	32.67
90	37.40	35.11	32.95

TABLE 8

Density of the Trichloroacetic Acid – Phenol System

C_6H_5OH (mole %)	Density		
	50°	70°	90°
10	—	1.562	1.541
20	—	1.511	1.486
25	1.508	—	—
30	1.477	1.458	1.435
40	1.426	1.410	1.382
50	1.373	1.351	1.328
60	1.324	1.289	1.270
70	1.253	1.238	1.207
80	1.207	1.175	1.150

TABLE 9

Viscosity of the Trichloroacetic Acid – Phenol System

C_6H_5OH (mole %)	Viscosity		
	50°	70°	90°
10	—	2.39	1.45
20	—	2.42	1.42
25	4.74	—	—
30	4.75	2.39	1.40
40	4.68	2.35	1.35
50	4.50	2.25	1.30
60	4.33	2.14	1.24
70	4.07	2.05	1.17
80	3.91	1.95	1.13

the additive towards greater values of surface tension. The increase in surface tension seems to indicate the existence of the compound $C_6H_5OH \cdot CCl_3COOH$ in the molten state.

The density of the mixtures (Table 8, Fig. 6) decreases from trichloroacetic acid to phenol; the density isotherms almost coincide with the additive line and give no indication of component reaction in the homogeneous, molten medium.

The viscosity isotherms (Table 9, Fig. 6) are S-shaped curves. Such curves belong to systems with chemical reaction [8 - 10]. It is noteworthy that the viscosity decreases by a factor of 3.5 with an increase in temperature from 50 to 90°; the S-shape of the curves becomes increasingly less with an increase in temperature and this indicates considerable dissociation of the compound in the molten, homogeneous medium.

In comparing the surface tension, density and viscosity isotherms of all three systems studied, one can see that the introduction of chlorine into the acetic acid radical results in greater chemical reactivity between phenol and the acetic acid derivatives.

SUMMARY

1. Binary systems composed of phenol and acetic acid and its chloro derivatives were investigated physicochemically through their density, viscosity and surface tension.

2. The density, viscosity and surface tension isotherms of systems composed of acetic and monochloroacetic acids and phenol gave no indication of the existence of a compound in the molten medium.

3. The viscosity and surface tension isotherms and the fusion diagram of the trichloroacetic acid – phenol system indicate the existence of the compound $C_6H_5OH \cdot CCl_3COOH$.

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INVESTIGATION OF CONTINUOUS TRANSITIONS FROM STABLE INTO METASTABLE PHASE SEPARATION

I.L. Krupatkin

The conversion of stable phase separation to the metastable state may be of practical interest as a method for obtaining alloys of two substances over the whole range of concentrations of the binary system formed by them. This problem is dealt with in a series of papers [1 - 4] in which the stable phase separation of a binary system is converted into a metastable state by adding a third component to it. It was shown that the continuous conversion that is described occurs in a ternary system through a cross section with a target and a point of contact of the fusion and phase separation curves. A series of basic forms of continuous conversions in the range of stable and metastable phase separation which may occur in ternary systems, as shown in Fig. 1 in the form of polythermal cross sections at mn of the prism of a ternary system A-B-C, may be derived for liquid phase equilibria with upper critical solution temperatures. Here, it is conditionally assumed that the A-B system is homogeneous in the liquid state, the A-C system has metastable phase separation and the B-C system has stable phase separation. The solid line on the cross sections b-e shows the polytherm of phase separation and the dotted line – the fusion polytherm of the A-B system (the fusion polytherm of the cross section mn may have the same form). The first form of the transition (b) is caused by a phase separation surface, without extreme and special points.

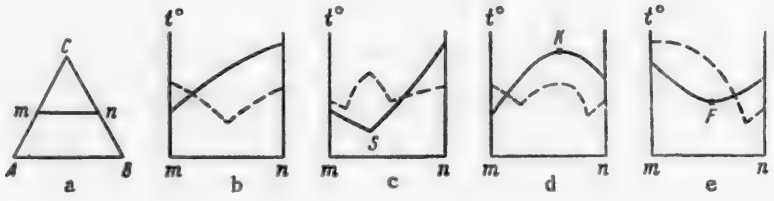

Fig. 1. Forms of continuous transitions from stable to metastable phase separation. Explanation in the text.

The benzoic acid – salicylic acid – water system has this form of transition [1]. A transition of the second form (c) arises from a singular arm (point S lies on this arm). An example of this is the salicylic acid – picric acid – water system [2]. A transition of the third form (d) arises from the triple critical point K of the phase separation surface. This form of transition has not been achieved completely experimentally; a case that is very close to it, when the phase separation surface does not quite reach the boundary of the B-C binary system, occurs in the antipyrine – salicylic acid – water system [3]. The fourth transition form (e) arises from a saddle point F in the phase separation surface.

This transition form has not yet been found experimentally and its detection is the purpose of this work. The transition forms indicated may have various variants due to the changes in the character of geometric elements or changes in the relative position of the fusion and phase separation surfaces. Thus in case (c) the singular arm may be anticlinic, in cases c, d and e the singular arm and critical and saddle points may be either in the region of stable or metastable liquid phase equilibria.

EXPERIMENTAL

Salicylic acid – phenol – water and anthranilic acid – phenol – water ternary systems were used to achieve experimentally continuous reciprocal transitions from stable and metastable phase separation through a saddle point. The binary systems forming them were characterized by the following data. The phenol – water system was investigated by means of its fusion and phase separation [5]. The stable phase separation curve found has an upper critical point at 66°, which corresponds to 34% phenol; the monotectic equilibrium is at 12.2°. The salicylic acid – water system was investigated by means of its fusion and phase separation [6]. The metastable phase separation curve has an upper critical point at 89.1° (32% salicylic acid). The crystallization curve of the acid above the phase separation curve has a horizontal section at 104°. The anthranilic acid – water system was studied by means of its fusion and phase separation [7]. The upper critical point of the metastable phase separation curve at 78° corresponds to a 38% anthranilic acid content in the mixture. The crystallization curve of the anthranilic acid above the phase separation curve has a horizontal section at 105°. There is no data in the literature on systems formed by these acids and phenol. In the present work we attempted to investigate these systems by means of their fusion, though, due to the great viscosity of the mixtures of salicylic acid and phenol only part of the fusion diagram was studied and only separate points of the anthranilic acid – phenol system were obtained. The fusion curve of the first system did not indicate the formation of a compound. In spite of that, the tendency of the ortho derivatives of benzoic acid examined for complex formation suggested the formation of unstable complexes between them and phenol and this was confirmed by the present work. Thus, the presence of two binary systems with stable and metastable phase separation and a third with the formation of a dissociating complex in each of the ternary systems being studied made it possible to achieve transitions of the fourth form (d) in them.

TABLE 1

Equilibrium in the Salicylic Acid – Phenol System

Salicylic acid (weight %)	Crystallization temperature
26.85	76.0°
30.00	95.0
41.60	108.5
60.00	125.0
80.40	141.5
100.00	155.0

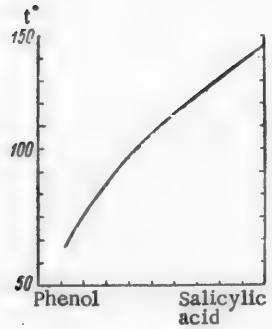

Fig. 2. Crystallization in the salicylic acid – phenol system

In the work we used the following substances: distilled phenol, a fraction boiling at 181° (m.p. 42°), salicylic and anthranilic acids of analytical purity with m.p. 155 and 145°, respectively, and doubly distilled water. The systems were investigated by means of their phase separation by the visual polythermal method of V.F. Alekseev [8] in sealed glass ampules in an oil thermostat. Investigation by means of their fusion was carried out by two methods in parallel – by Shreder's method [9] and by internal seeding [10].

The salicylic acid-phenol system was investigated by means of its fusion (Table 1, Fig. 2). The mixtures located close to phenol did not crystallize and, therefore, there is no data on them. Figure 2 shows that the crystallization curve of salicylic acid did not have either extreme or other special points.

The salicylic acid – phenol – water* ternary system was studied by means of its phase separation (Table 2). Six polythermal cross sections of its temperature–concentration prism, going from the water arm to the boundary of the salicylic acid – phenol binary system were investigated (Table 2, Fig. 3). Figure 3 gives the fusion curve K_p and the phase separation curve P_a of the salicylic acid – water system and the phase separation curve aKb of the phenol – water system and the line of its monotectic equilibrium ab. As in the phase separation curves of binary systems, the reciprocal solubility polytherms of the liquid phases of a ternary system have upper critical solution temperatures. The latter descend from the critical points K and K_1 of phase-separating binary systems when the cross sections move into the prisms of ternary systems. Due to this, a saddle point forms on the phase separation surface of the ternary system between the fifth and sixth cross sections. It is found at 61.5° and a composition of 9% salicylic acid, 26% phenol and 65% water.

*E.F. Leshchinskii participated in the investigation.

TABLE 2

Polytherms of the Salicylic Acid (SA) – Phenol (P) – Water System

Cross section 1: 20% P, 80% SA		Cross section 2: 40% P, 60% SA		Cross section 3: 50% P, 50% SA	
water (weight %)	phase separation temperature	water (weight %)	phase separation temperature	water (weight %)	phase separation temperature
33.00	50.0°	34.00	47.0°	34.50	47.5°
36.00	60.0	40.00	58.0	39.63	56.5
41.21	65.0	45.00	63.0	40.00	64.0
45.23	69.0	52.00	67.0	55.60	65.5
56.65	75.0	61.70	81.5	65.00	66.0
61.85	75.5	70.00	69.0	72.43	66.0
71.23	76.0	80.42	69.0	80.67	65.0
80.03	76.0	90.73	64.0	88.88	62.0
90.61	72.0	94.50	47.0	92.00	55.0
94.16	60.0			94.00	47.0
95.07	50.0				

Cross section 4: 56.5% P, 43.5 % SA		Cross section 5: 60% P, 40% SA		Cross section 6: 80% P, 20% SA	
36.00	48.0°	38.00	46.5°	40.10	49.0°
40.65	57.0	41.55	52.5	45.00	55.0
52.51	63.0	48.00	60.0	50.96	59.0
63.50	65.0	51.64	62.5	60.03	62.0
67.72	65.0	60.42	63.0	70.43	62.0
69.04	65.0	67.37	63.0	80.02	61.0
80.86	64.0	71.87	63.0	85.00	55.0
91.32	56.0	80.14	62.5	90.04	48.0
93.06	51.5	91.39	54.0		
94.00	46.0	92.94	48.0		

The highest crystallization temperatures in the phase-separating mixtures of the cross sections are at 93, 84, 79, 74, 72 and 37° respectively in the 1, 2, 3, 4, 5 and 6 cross sections. These data show that phase separation is metastable in cross sections 1 – 5 and stable only in cross section 6. Thus, the saddle point of the given system should be located in the region of metastable liquid phase equilibria. In accordance with this, the crystallization surface, starting from the boundary of the salicylic acid – water system, must at first slope upwards but close to the boundary of the phenol – water system it will descend sharply.

Seven phase separation isotherms were plotted for the salicylic acid – phenol – water ternary system, given in Fig. 4, from the experimentally obtained polytherms. The isotherms at 85 - 62°, i.e., at high temperatures, limit phase separation into two separate regions which start at the solubility cross sections of the two binary systems. At 61.5° the phase separation regions abut on saddle point C. At 60 - 50°, i.e., at low temperatures, the isotherms form curves with reciprocal solubility maxima for the liquid phases. The isotherms maxima and the saddle point in the salicylic acid – phenol binary system are at 27% salicylic acid and 73% phenol. This composition corresponds to a complex with a 1:4 molecular ratio of these components. Consequently, the salicylic acid – phenol system is the dominating system in the ternary system being studied. The instability of the complex formed and its strong dissociation in water explain its greater solubility in water than those of its components and causes the formation of maxima on the phase separation isotherms and then the saddle point. An increase in the temperature intensifies these processes and results in a division of the phase separation region of the ternary system into two. In this way, a continuous transition of the stable phase separation of the phenol – water system into the metastable one of salicylic acid – water through a saddle point is achieved in the ternary system described (case e, Fig. 1).

Anthranilic acid – phenol – water ternary system. Table 3 gives the results of studying the polythermal cross sections through the temperature-concentration prism, going from the water arm to the boundary of the anthranilic acid – phenol binary system. Figure 5 shows the fusion curve K_p and the phase separation curve P_a of the anthranilic acid – water system and also the phase separation curve aKb and monotectic equilibrium line ab of the phenol – water system. The upper

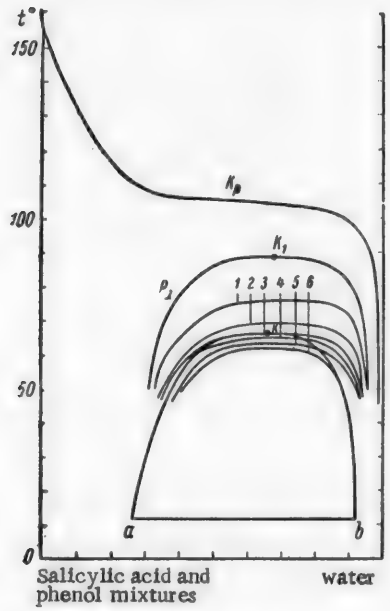

Fig. 3. Polytherms of the salicylic acid – phenol – water system. Explanation in the text.

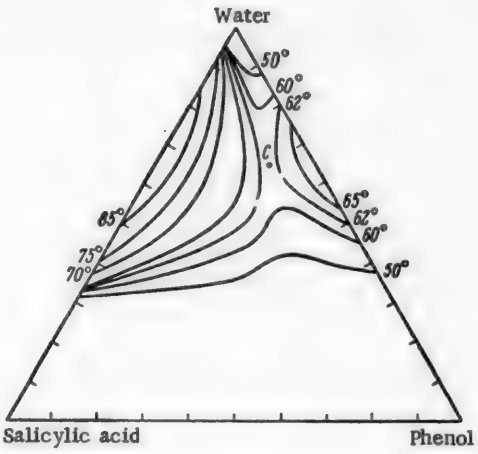

Fig. 4. Phase separation isotherms of the salicylic acid – phenol – water system. Explanation in the text.

critical solution temperatures decrease from the critical points K and K_1 of the binary systems formed with water, as the cross sections move into the prism of the ternary system. Due to this a saddle point forms on the phase separation surface of the ternary system between the 3rd and 4th cross sections. This point is at 63.5° and corresponds to 10% anthranilic acid, 27% phenol and 63% water.

Six phase separation isotherms of the anthranilic acid – phenol – water ternary system were plotted from the experimentally obtained polytherms and are shown in Fig. 6. The isotherms located above the saddle point (at temperatures of 73 - 64°) and the corresponding binary system conoids together limit to two the separate phase separation regions which abuton saddle point C at 63.5°. The isotherms located below the saddle point (at temperatures of 62 - 60°) are curves with maxima of reciprocal solubility of the liquid phases. The isotherm maxima and the saddle point in the anthranilic acid – phenol binary system are at 27% anthranilic acid and 73% phenol. This composition corresponds to a complex with a 1:4 molecular ratio. Consequently, the anthranilic acid – phenol system is the dominating system in the given ternary system. The formation of a complex in the dominating system and its decomposition in water explain the formation of the saddle point. Thus, continuous transition of a stable phase separation of the phenol – water system through a saddle point into the metastable one of the anthranilic acid – water system occurs in the anthranilic acid – phenol – water ternary system, i.e., case e, Fig. 1. It is interesting that in the dominating systems of both ternary systems studied a complex is formed with the same molecular ratio of the components. The great similarity of the phase separation diagrams of the ternary systems studied indicates that the properties of the two complexes are also analogous. This is explained by the similarity of the properties of the chemical components forming the complexes.

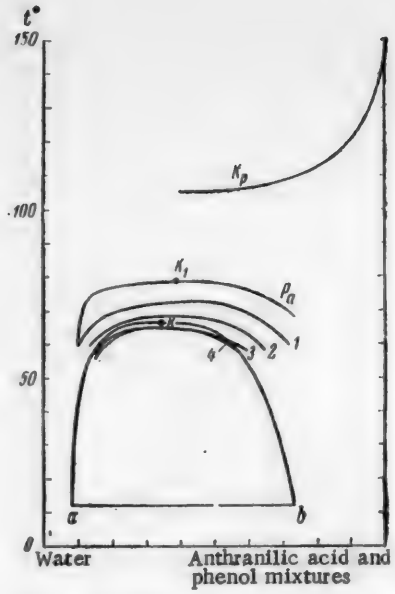

Fig. 5. Polytherms of the anthranilic acid – phenol – water system. Explanation in the text.

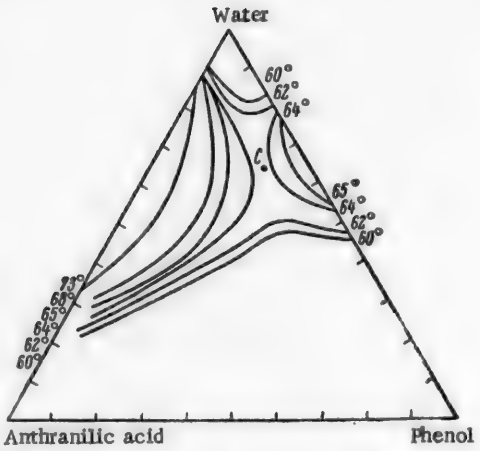

Fig. 6. Phase separation isotherms of the anthranilic acid – phenol – water system. Explanation in the text.

TABLE 3

Polytherms of the Anthranilic Acid (AA) – Phenol (P) – Water System

Cross section 1: 20% P, 80% AA		Cross section 2: 40% P, 60 % AA	
water (weight %)	phase separation temperature	water (weight %)	phase separation temperature
30.00	62.0°	35.00	58.0°
40.00	69.0	40.00	63.0
51.00	72.5	50.00	66.5
60.00	73.0	60.00	68.5
70.00	71.0	70.00	67.0
80.00	69.0	80.00	65.5
90.00	59.0	85.00	61.0

Cross section 3: 60% P, 40% AA		Cross section 4: 80% P, 20% AA	
40.00	58.0°	43.00	58.0°
48.00	63.0	50.00	62.0
56.00	64.0	60.00	64.5
60.00	64.0	70.00	64.5
70.00	64.0	80.00	61.0
80.00	62.0	85.00	55.0
85.00	56.5		

SUMMARY

1. The forms of continuous reciprocal transitions of metastable and stable phase separation of binary and ternary systems were examined. They were reduced to four basic types.

2. The components of the salicylic acid – phenol binary system, studied by means of its fusion, did not react chemically.

3. The salicylic acid – phenol – water and anthranilic acid – phenol – water ternary systems were studied by means of their phase separation. It was found that in both cases the phase separation volume of the ternary system combines the phase separation planes of the two binary systems formed with water and has a saddle point. The reasons for the formation of such forms of diagram for ternary systems were explained. It was shown that in both ternary systems investigated one of the forms of continuous reciprocal transition of metastable and stable phase separation of binary systems occurred with this transition passing through a saddle point.

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TERNARY RECIPROCAL SYSTEM OF LITHIUM AND SODIUM FORMATES AND NITRATES

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The system of lithium and sodium formates and nitrates is the first to be investigated in the systematic study of systems of lithium salts of aliphatic acids and lithium and sodium nitrates.

Work carried out by A.G. Bergman et al. [1] showed that in some systems with lithium salts, the direction of the exchange reaction does not correspond to its conventional thermochemical effect; this makes the study of systems with lithium salts much more interesting.

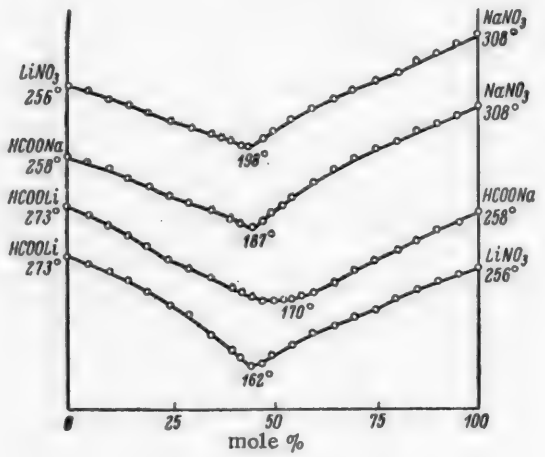

Fig. 1. Fusion curves of binary systems

A visual polythermal method was used for the investigation. The temperature was measured with a nichrome-constantan thermocouple. The fusion was carried out in a test tube which was placed in a larger test tube for even heating. The melts were mixed manually with a glass mixer. The calibration curve was plotted from the boiling point of water and the melting points of benzoic acid (122.5°), mannitol (166°), succinic acid (183°), sodium nitrate (308°) and potassium nitrate (337°). Analytically pure grades of salt were purified by 2 recrystallizations. The melting points of the salts were: 308° for sodium nitrate, 256° for lithium nitrate and 258° for sodium formate. The lithium formate decomposed when heated and its melting point was determined by extrapolation using the binary systems: lithium formate – sodium formate and lithium nitrate – lithium formate. It was found to be 273°.

According to the literature data, polymorphous conversions are known for sodium nitrate at 275° [2] and sodium formate at 242° [3]. The composition is expressed everywhere in molar percent.

Binary systems. According to data in [4] the sodium nitrate – lithium nitrate system forms a continuous series of solid solutions. According to later data [5], the system has a eutectic containing 41.5% $NaNO_3$ with

m.p. 195° or, according to data [6], 43.75% sodium nitrate with m.p. 196°. According to our data, the eutectic point corresponds to 45% $NaNO_3$ and 198°.

TABLE 1

Binary Systems

$LiNO_3$—$NaNO_3$		$LiNO_3$—HCOOLi		HCOOLi—HCOONa		HCOONa—$NaNO_3$	
mole % $NaNO_3$	temperature	mole % HCOOLi	temperature	mole % HCOOLi	temperature	mole % $NaNO_3$	temperature
0	256°	0	256°	0	258°	0	258°
5	250	5	247	5	250	5	252
10	242	10	238	10	242	10	245
15	236	15	228	15	232	15	236
20	230	20	220	20	224	20	226
25	224	25	212	25	214	25	219
30	216	30	206	30	204	30	212
35	210	35	196	35	194	35	204
40	204	40	188	40	182	40	196
45	198	45	180	45	176	45	188
50	208	50	170	50	170	50	192
55	219	55	162	55	175	55	210
60	230	60	178	60	184	60	226
65	240	65	194	65	196	65	240
70	250	70	208	70	208	70	250
75	260	75	220	75	220	75	260
80	270	80	232	80	232	80	270
85	280					85	278
90	290					90	288
95	300					95	298
100	308					100	308

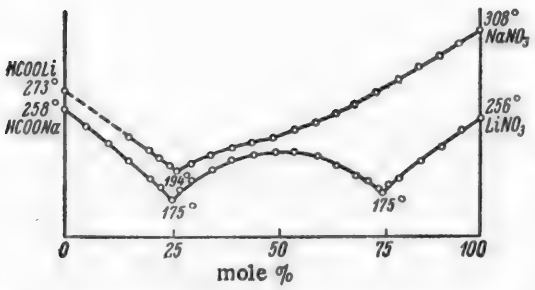

Fig. 2. Diagonal cross sections of the ternary reciprocal system.

The lithium nitrate – lithium formate system was first investigated by us. The eutectic point corresponds to 55% lithium formate and 162°. The system was studied up to 80% lithium formate.

The sodium formate – lithium formate system was first investigated by N.M. Sokolov [3]. According to our data, the system forms solid solutions at a minimum m.p. of 170° at 50% sodium formate.

According to our measurements the sodium nitrate – sodium formate system [3] has a eutectic containing 48% sodium nitrate with m.p. 187° (Table 1, Fig. 1).

Diagonal cross sections. The sodium formate – lithium nitrate diagonal cross section is not stable. The branches of the first crystals of the components go down to 175° and intersect the branch of the exchange product in two eutectic points at 24 and 76% lithium nitrate.

The sodium nitrate – lithium formate diagonal cross section was studied up to an 80% lithium formate content. In the section studied, its diagram consists of two branches which intersect at the eutectic point at 194° and 26% sodium nitrate (Table 2, Fig. 2). We consider this diagonal cross section to be stable.

Internal cross sections. The internal cross sections were studied to find the limits of the fields of first crystallization. The directions of the cross sections are shown in Fig. 3 and their characteristics are given in Fig. 4.

TABLE 2

Diagonal Cross Sections

$LiNO_3$—HCOONa				$NaNO_3$—HCOOLi			
mole % HCOONa	temperature	mole % HCOONa	temperature	mole % $NaNO_3$	temperature	mole % $NaNO_3$	temperature
0	256°	55	220°	20	225°	60	235°
5	245	60	215	25	196	65	242
10	230	65	208	26	194	70	246
15	212	70	190	30	197	75	254
20	194	75	175	35	204	80	264
24	175	80	192	40	208	85	272
25	180	85	210	45	215	90	284
30	196	90	230	50	222	95	294
35	204	95	242	55	228	100	308
40	214	100	258				
45	220						
50	222						

A stable diagonal cross section divides the square of the system into two phase triangles: 1) lithium nitrate – sodium nitrate – lithium formate and 2) sodium nitrate – sodium formate – lithium formate. The first phase triangle has a triple point at 146°, 14% sodium nitrate, 46% lithium nitrate and 40% lithium formate. In the second phase triangle the triple point lies at 154°, 14% sodium nitrate, 49% lithium formate and 37% sodium formate.

The diagram of the ternary reciprocal system has five crystallization fields. The areas of these fields (in percent of the total area of the square) consist of: sodium nitrate 57.13, lithium formate 13.92, lithium nitrate 13.80, sodium formate 12.16; 3% is taken up by the field of the HCOOLi – HCOONa solid solutions, which decompose when more than 5% of a third component is added.

The results of the experimental data are generalized in the form of isotherm projections on the square of the system (Fig. 5). The positions of invariant points and cocrystallization lines are given in the form of the projection of these points on the HCOOLi – HCOONa side (Fig. 6).

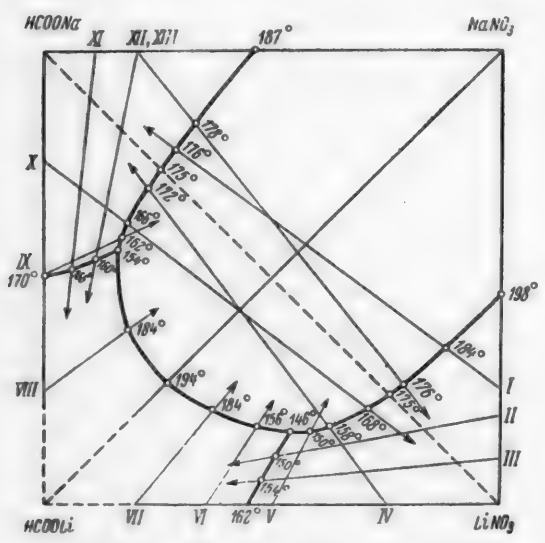

Fig. 3. The direction of internal cross sections

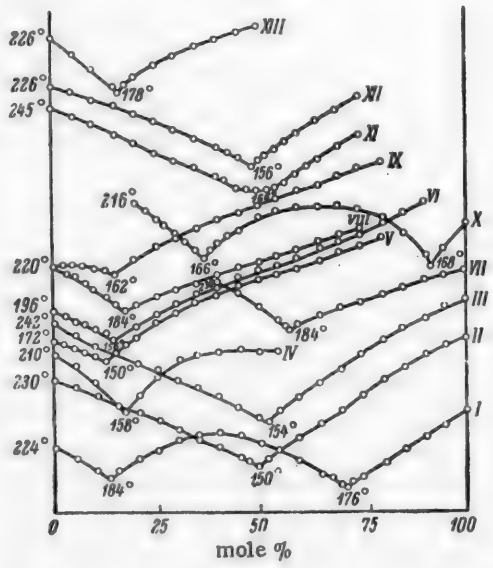

Fig. 4. Characteristics of the internal cross sections

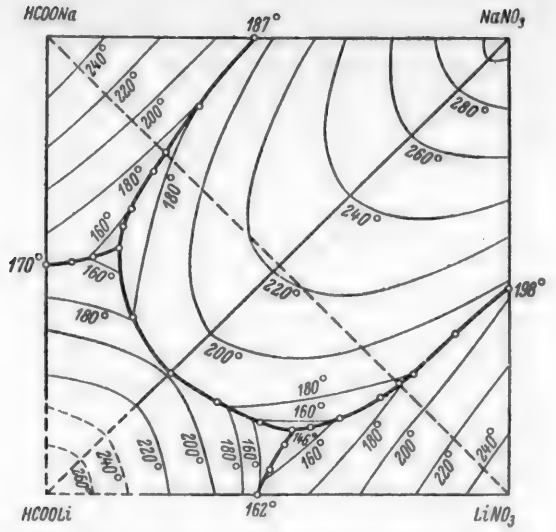

Fig. 5. Projection of the reciprocal system diagram on the composition square.

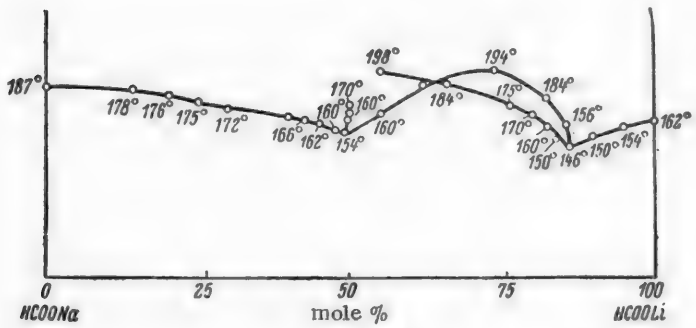

Fig. 6. Projection of the cocrystallization line on the HCOOLi – – HCOONa side.

SUMMARY

1. The ternary reciprocal system of lithium and sodium formates and nitrates was investigated by a visual polythermal method and, according to the classification of A.G. Bergman and N.S. Dombrovskaia [7], this system is an irreversible reciprocal system.

2. The chemical exchange equilibrium in the system is displaced toward lithium formate and sodium nitrate, which are the most refractory of the system's components.

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THE MOLECULAR REFRACTION OF CERTAIN CLASSES OF ALKYLTHIOPHENES AND ALKYLTHIACYCLOALKANES

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A knowledge of the physical properties of alkylthiophenes and alkylthiacycloalkanes is of great value practically. In spite of this, many of them have not been investigated at all [1].

A method, proposed by one of the authors of this article [2 - 7] makes it possible to fill in this gap rapidly.

In previous reports [8] a general formula was proposed for determining the standard molar specific heats, entropies and heats of formation of gaseous and liquid 3-thiaalkanes, 2-thiaalkanes, 1-alkanethiols and 3,4-dithiaalkanes.

Single formulas are proposed in this article for determining the molecular refraction R_D of alkylthiophenes, alkylthiacyclopropanes, alkylthiacyclopentanes and alkylthiacyclohexanes, on which there is no data in the literature [1].

It is known that in homologous series of organic compounds which form a ring (cylopentane, cyclopropane etc), many properties are practically completely additive in terms of methylene groups (CH_2) from the second member of the series onwards. This is easily demonstrated for molecular refraction R_D.

As an example let us calculate the molecular refraction of the lower 2-alkylthiophenes from the molecular refraction of 2-propylthiophene, which is 38.64 at 20° [1]. Then, subtracting the portion of R_D that may be assigned to one CH_2 group (4.635) we obtain: 34.005 for 2-ethylthiophene, 29.37 for 2-methylthiophene and 24.735 for thiophene. The values obtained differ by 0.095, 0.08 and 0.37, or 0.3, 0.25 and 1.5%, respectively from the experimental values for the molecular refractions of these compounds. This shows that as one proceeds further from the beginning of the 2-alkylthiophene series, the deviation from additivity decreases rapidly and that of the third member is only 0.095 or 0.3%. One naturally expects practically complete additivity starting from 2-butylthiophene. A check shows that the same situation occurs in 3-alkylthiophenes, alkylthiacycloalkanes and others. Using the values given in [1] for the molecular refraction of the third and especially the fourth member of an homologous series of organosulfur compounds, this makes it possible to obtain general rules for determination of the R_D of all the other members of the particular series of compounds (with the exception of the starting members).

Analyzing the molecular refraction, R_D, of some alkylthiophenes and alkylthiacycloalkanes given in [1] using the above method, we found the following general formulas for determining molecular refractions R_D.

2-Alkylthiophenes and 3-alkylthiophenes:

$$R_D = 24.735 - 0.06\,(r - 1) + 4.635 \cdot z \text{ at } 20^\circ \quad (z \geq 1) \tag{1}$$

$$R_D = 24.755 - 0.06\,(r - 1) + 4.635 \cdot z \text{ at } 25^\circ \quad (z \geq 1) \tag{2}$$

2-Isoalkyl- and 3-isoalkylthiophenes:

$$R_D = 24.705 - 0.13\,(r - 1) + 4.635 \cdot z \text{ at } 20^\circ \quad (z \geq 1) \tag{3}$$

$$R_D = 24.715 - 0.13\,(r - 1) + 4.635 \cdot z \text{ at } 25^\circ \quad (z \geq 1) \tag{4}$$

TABLE 1

Molecular Refractions of Some Alkylthiophenes and Alkylthiacyclopropanes

Name of alkylthiophene	Chemical formula	20°			Name of alkylthiacyclopropane	Chemical formula	20°		
		calculated by formulas (1) - (4)	data from [1]	Δ			calculated by formula (9)	data from [1]	Δ
Thiophene	C_4H_4S	24.735	24.365	+ 0.37	Thiacyclopropane	C_2H_4S	17.33	17.2	+ 0.13
2-Methylthiophene.	C_5H_6S	29.37	29.29	+ 0.08	2-Methylthiacyclopropane. . . .	C_3H_6S	21.96	22.1	− 0.14
2-Ethylthiophene.	C_6H_8S	34.00	33.91	+ 0.09	2-Ethylthiacyclopropane.	C_4H_8S	22.60	26.6	0.0
2-Propylthiophene	$C_7H_{10}S$	38.64	38.64	0.00	2-Butylthiacyclopropane.	$C_5H_{10}S$	31.24		
2-Butylthiophene.	$C_8H_{12}S$	43.28			2-Pentylthiacyclopropane	$C_6H_{12}S$	35.87		
2-Pentylthiophene etc.	$C_9H_{14}S$	47.91			2-Hexylthiacyclopropane	$C_7H_{14}S$	40.50		
3-Methylthiophene.	C_5H_6S	29.31	29.225	+ 0.095	2-Heptylthiacyclopropane. . . .	$C_8H_{16}S$	45.14		
3-Ethylthiophene.	C_6H_8S	33.94	33.88	+ 0.06	2-Octylthiacyclopropane.	$C_9H_{18}S$	49.78		
3-Propylthiophene	$C_7H_{10}S$	38.58	38.58	0.00	2-Nonylthiacyclopropane etc. .	$C_{10}H_{20}S$	54.11		
3-Butylthiophene.	$C_8H_{12}S$	43.22							
3-Pentylthiophene	$C_9H_{14}S$	47.85							
3-Hexylthiophene etc.	$C_{10}H_{16}S$	52.48							
2-Isopropylthiophene etc. . .	$C_7H_{10}S$	38.61	38.61	0.00					
Per CH_2 group . .		4.635			Per CH_2 group .		4.635		

TABLE 2

Molecular Refractions of Some Alkylthiacyclohexanes and Alkylthiacyclopentanes

Name of alkylthiacyclohexane	Chemical formula	20°			Name of alkylthiacyclopentane	Chemical formula	20°		
		calculated by formula (5)	data from [1]	Δ			calculated by formula (7)	data from [1]	Δ
2-Methylthiacyclohexane . . .	$C_6H_{12}S$	35.67	35.67	0.00	Thiacyclopentane	C_4H_8S	26.330	26.179	+ 0.121
3-Methylthiacyclohexane . . .	$C_6H_{12}S$	35.62	35.61	+ 0.01	2-Methylthiacyclopentane . . .	$C_5H_{10}S$	30.965	30.98	− 0.015
4-Methylthiacyclohexane . . .	$C_6H_{12}S$	35.57	35.62	− 0.05	3-Methylthiacyclopentane . . .	$C_5H_{10}S$	30.765	30.80	− 0.035
2-Ethylthiacyclohexane.	$C_7H_{14}S$	40.30			2-Ethylthiacyclopentane.	$C_6H_{12}S$	35.60	35.6	0.0
3-Ethylthiacyclohexane.	$C_7H_{14}S$	40.26			3-Ethylthiacyclopentane.	$C_6H_{12}S$	35.40	35.4	0.0
4-Ethylthiacyclohexane.	$C_7H_{14}S$	40.20			2-Propylthiacyclopentane	$C_7H_{14}S$	40.24		
2-Propylthiacyclohexane. . . .	$C_8H_{16}S$	44.94			3-Propylthiacyclopentane	$C_7H_{14}S$	40.04		
3-Propylthiacyclohexane. . . .	$C_8H_{16}S$	44.89			2-Butylthiacyclopentane.	$C_8H_{16}S$	44.87		
2-Butylthiacyclohexane.	$C_9H_{18}S$	49.58			3-Butylthiacyclopentane.	$C_8H_{16}S$	44.67		
3-Butylthiacyclohexane.	$C_9H_{18}S$	49.52			2-Pentylthiacyclopentane	$C_9H_{18}S$	49.50		
2-Pentylthiacyclohexane etc .	$C_{10}H_{20}S$	54.21			3-Pentylthiacyclopentane	$C_9H_{28}S$	49.30		
					2-Hexylthiacyclopentane etc. .	$C_{10}H_{20}S$	54.14		
Per CH_2 group . .		4.635			Per CH_2 group . .		4.635		

2-Alkyl-, 3-alkyl- and 4-alkylthiacyclohexanes:

$$R_D = 31.035 - 0.05\,(r-1) + 4.635 \cdot z \text{ at } 20^\circ \quad (z \geq 1) \tag{5}$$

$$R_D = 31.045 - 0.05\,(r-1) + 4.635 \cdot z \text{ at } 25^\circ \quad (z \geq 1) \tag{6}$$

2-Alkyl- and 3-alkylthiacyclopentanes:

$$R_D = 26.33 - 0.2\,(r-1) + 4.635 \cdot z \text{ at } 20^\circ \quad (z \geq 1) \tag{7}$$

$$R_D = 26.343 - 0.113\,(r-1) + 4.635 \cdot z \text{ at } 25^\circ \quad (z \geq 1) \tag{8}$$

2-Alkylthiacyclopropanes:

$$R_D = 17.33 + 4.635 \cdot z \qquad \text{at } 20^\circ \quad (z \geq 1) \tag{9}$$

$$R_D = 17.34 + 4.635 \cdot z \qquad \text{at } 25^\circ \quad (z \geq 1) \tag{10}$$

In formulas (1) - (10) z is the number of methylene groups or carbon atoms in the linear carbon chain C-C-C. . . of a molecule of the appropriate compound; r is the number of carbon atoms in the ring from which the C-C-C chain starts.

The reliability of the results depends on the accuracy of the molar refraction values for 2- and 3-propylthiophene, 2-, 3- and 4-ethylthiacyclohexanes and 2- and 3-ethylthiacyclopentanes, taken from [1] and used for deriving the equations given above. However, if it is found later that the initial values are greater than the true ones by a term δ, this may readily be taken into account in formulas (1) - (10) by adding δ to the first term in the right section. Furthermore, the accuracy of the formulas depends on the amount the initial value of R_D of 2-propylthiophene and others is less than its additive value. The error, due to this reason, is not greater than 0.2 – 0.3%.

In Tables 1 and 2 are given the molecular refractions at 20° for a series of alkylthiophenes and alkylthiacycloalkanes. Most of them are presented for the first time. Some of them are compared with the existing literature data found in [1]. As can be seen, the values of molecular refractions calculated by our formulas agree very well with the experimental data.

SUMMARY

1. General formulas are derived for determining the values of molecular refractions, R_D, at 20 and 25° for 2-alkylthiophenes, 3-alkylthiophenes, 2-isoalkylthiophenes and 3-isoalkylthiophenes, with an accuracy of the order of 0.2 – 0.3% if one considers the data in [1] as correct.

2. General formulas are proposed for determining the values of molecular refraction, R_D, at 20 and 25° for 2-alkyl-, 3-alkylthiacyclopentanes, for 2-alkyl-, 3-alkyl- and 4-alkylthiacyclohexanes and for 2-alkyl- and 3-alkylthiacyclopropanes. The accuracy is of the order of 0.2 – 0.3%, if the initial data in [1] are considered correct.

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DISCUSSION

CONCERNING THE PAPERS OF L.M. LITVINENKO, R.S. CHESHKO, S.V. TSUKERMAN, A.D. GOFMAN, B.M. KOLESNIKOVA AND OTHERS ON "SPATIAL STRUCTURE AND REACTIVITY"

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A series of papers [1 - 3] under the title of "Spatial Structure and Reactivity" was published in Vol. 27 of the Journal of General Chemistry.

The objective of the authors was to solve the extremely topical problem of the transmission of the reciprocal effects in molecules with conjugated bonds across atoms of oxygen, sulfur, etc., included in the conjugated system. The rate of acylation of 4-aminobiphenyl, 4-aminodiphenyl oxide, 4-aminodiphenyl sulfide and their 4'-derivatives was measured in these investigations, using 4-nitrobenzoyl chloride as the acylating agent. It was shown that the introduction of a nitro group in the 4'-position of the compounds in question considerably slowed down the acylation process, and the magnitude of this retarding effect decreased in the following order: diphenyl sulfide > diphenyl oxide > biphenyl.

On the basis of these facts the authors inferred that the molecular systems of diphenyl oxide and diphenyl sulfide are – in spite of the oxygen and sulfur bridges between their benzene rings – better transmitters of the electronic interaction of the substituents than the biphenyl system in which these rings are directly linked. This conclusion is not adequately proven.

In considering the experimental data, the authors did not take into account the differences in the spatial configuration of biphenyl derivatives (linear) on the one hand and that of diphenyl oxide and diphenyl sulfide (angular) on the other. Moreover, the considerable drop in the rate of reactions in 4'-nitro derivatives in comparison with unsubstituted compounds in the case of diphenyl oxide and diphenyl sulfide may be caused by steric hindrance.

The crux of the matter is that the distance between N and N' in 4'-nitro-4-amino-substituted diphenyl oxide and diphenyl sulfide (8 – 8.5 A) is comparable with the distance between the end groups of the acylating agent – 4-nitrobenzoyl chloride (7.5 – 7.8 A), so that the introduction into the 4' position of a polar group (NO_2) considerably reduces the probability that a reaction will take place with substances containing similarly oriented polar groups (NO_2, COCl). These hindrances are absent in the case of biphenyl derivatives. The observed fall in reaction rate of disubstituted diphenyl oxides and diphenyl sulfides in comparison with monosubstituted derivatives is evidently due to a considerable extent to steric factors rather than to the conditions of transmission of the reciprocal influence of the substituents.

Most of the physicochemical data (ultraviolet absorption spectra, dipole moments, etc.) indicate that transmission of the reciprocal influence of substituents through sulfur atoms is hindered in aromatic compounds. This statement is supported by structural investigations on diphenyl sulfide derivatives. According to x-ray analyses [4] the 4,4'-dibromodiphenyl sulfide molecule is not planar, the benzene rings being at an angle towards one another, and the angle formed with the plane of the sulfur and bromine atoms is approximately 40°. Such a molecular configuration does not facilitate transmission of the reciprocal influence of substituents from one ring to the other.

Since the material in the cited papers indicates that work will continue in the field of application of chemical methods to the solution of the problem of transmission of reciprocal effects across heteroatoms, it seemed to us necessary to make our observations.

A solution of the problem in question calls for more extensive use of physical methods of investigation and a comprehensive study of the behavior of similar molecules.

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.